THE FATE OF SELECTED HEAVY METALS AND THEIR EFFECT ON THE ACTIVATED SLUDGE

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Dedicated to my wife, Zahra, my son Salman, and

my daughter, Zahra

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Cd - Cadmium

COD - Chemical oxygen demand

CST - Capillary suction time

F - Flow rate

F/M - Food to microorganism ratio - $\frac{FSi}{XV}$

Fw - Waste sludge flow

k - Maximum substrate utilization rate

k_B - Kincannon and Stover saturation constant

k_d - Maintenance energy or decay coefficient

k'_e - Eckenfelder's second order substrate removal rate constant

k_s - Waste concentration at which the rate of waste utilization is one-half the maximum rate

MLSS - Mixed liquor suspended solids

N - Number of observations

Pb - Lead

SD - Standard deviation

Se - Effluent substrate concentration

Si - Influent substrate concentration

SRT - Solids retention time

SVI - Sludge volume index

t - Hydraulic detention time

TOC - Total organic carbon

U - $\frac{(Si-Se)}{Xt}$, specific substrate utilization rate

U_{max} - Maximum substrate utilization rate

V - Reactor volume

X - Biological solids

X_e - Effluent suspended solids

X_r - Underflow solids concentration

Y_t - Trie uoe;d

Θ_c - SRT

Zn - Zinc

ZSV - Zone settling velocity

CHAPTER I

INTRODUCTION

Heavy metals are presently receiving remarkable attention because of their hazardous potential at low concentration. For example, cadmium produces kidney, cardiovascular, and respiratory diseases (1). Consequently, regulatory authorities are establishing extremely low allowable concentrations of heavy metals in effluent discharges to receiving waters.

The presence of heavy metals in municipal and industrial wastewaters have made the ultimate discharge of wastewaters a difficult task; because these heavy metals are discharged directly to a water course, they may exert toxic effects on aquatic life, concentrate in the food chain, and render the stream less useful to man. With more and more industrialization of developing countries it has become increasingly important to recycle and reuse the water. This has led to the necessity for removal of heavy metals.

Many municipal and industrial wastewater treatment plants employ some form of biological treatment process for the stabilization of organic and inorganic contaminants. It is necessary to assess the response of these processes receiving wastewaters containing heavy metals, because it is very important for design and operation. By knowing the approximate removal of heavy metals by biological systems, pre-treatment or post-treatment facilities can subsequently be designed

to meet the required discharge criteria.

Cadmium (Cd^{+2}), lead (Pb) and zinc (Zn) were selected for this research because of their widespread industrial use.

The purpose of this research was to study the fate of selected heavy metals and their effect upon the performance of a completely mixed activated sludge process.

CHAPTER II

LITERATURE REVIEW

Heavy metals may be removed by conventional sewage treatment plants in two stages. Primary settling may remove a portion of the metals which are either insoluble or adsorbed on the particles (2, 3). Further removal may occur in the activated sludge process (secondary biological treatment) by adsorption onto the sludge flocs (3, 4). It has been reported (4, 5, 6, 7) that activated sludge may be more efficient in removing metals than primary settling.

Oliver and Cosgrove (3) studied the efficiency of heavy metal removal by a conventional activated sludge treatment plant. Their results are shown in Table I. They found that most of the reduction in the dissolved heavy metals occurred in the aeration tank by adsorption on the biological floc. However, some of the dissolved metals were removed by primary treatment. The removal efficiency of the system for Ni and Mn was poor.

Jackson et al. (8) surveyed metals removed by activated sludge and reported copper removals ranging from 54 to 93%, chromium removals from 10 to 100%, and zinc removals from 60 to 100%. Total influent metal concentrations were less than 10 mg/l.

The removal efficiencies of metals by activated sludge treatment plants, activated sludge pilot plants, and laboratory scale activated sludge units have been summarized by Brown and Leater (9). This summary

is shown in Table II. This summary shows that metal removal efficiencies may be extremely high on occasion. It appears from the results presented that iron, copper, chromium and zinc showed the highest metal removal efficiencies. Nickel, manganese, calcium, and magnesium showed the lowest average removal efficiencies.

TABLE I

APPARENT REMOVAL EFFICIENCY OF DISSOLVED HEAVY METAL BY AN ACTIVATED SLUDGE TREATMENT PLANT*

Heavy Metal	Percentage Removal		
	Primary Treatment	Secondary Treatment	Overall Process
Cr	50	70	50
Cu	<1	56	59
Fe	20	33	47
Pb	<1	50	50
Mn	<1	<1	<1
Ni	<1	<1	<1
Zn	<1	30	30

*Adapted from (3)

Copper (Cu)

Principal sources of copper in industrial waste streams are from copper and brass manufacturing, copper sulfate production, electronics, and primary and secondary copper manufacturing.

Effects of Copper on the Activated Sludge Process

Previous investigators have concluded that copper is one of the

TABLE II

METAL REMOVAL EFFICIENCIES IN ACTIVATED SLUDGE TREATMENT PLANTS (ST), ACTIVATED SLUDGE PILOT PLANTS (PP) AND LABORATORY SCALE ACTIVATED SLUDGE UNITS (LS)

Reference	Source of Sample	Activated Sludge Influent (mg/l^{-1})	Range of Removal Efficiency (%)	Average Removal Efficiency (%)
		Aluminum		
10	ST	0.5-1.75	70-98	92
11	PP	0.25-0.35		51
		Cadmium		
10	ST	0.03-0.12	57-92	80
3	ST	0.002-0.01	51-100	50
12	ST	0.001-0.002	30-64	63
4	ST	0.018		11
7	ST	0.01-0.028		47
13	PP	0.018		51
14	PP	0.013		39
15	LS	0.012		26
			11-100+	46*
		Calcium		
11	PP	99-112	5-7	6
		Chromium		
10	ST	0.01-0.03	63-84	76
3	ST	0.03-0.8	75-99	54
16	ST	0.03	80-84	33
17	ST	0.06-0.09		70
4	ST	0.059		78
18	ST	4.4-38		88
7	ST	0.3-0.315		82
13	PP	0.079		61
2	PP	47		44
14	PP	0.215		57
15	LS	0.12		88
			33-99+	66*
		Copper		
10	ST	0.05-0.16	78-98	93
3	ST	0.04-0.66	70-90	60
12	ST	0.01-0.093	69-85	79
17	ST	0.06-0.12	75-79	55
4	ST	0.17	85-91	61
7	ST	0.1-0.13	70-86	77
13	PP	0.098	55-92	43
19	PP	10-25		78
2	PP	9		75
14	PP	0.92		33
20	LS	2.1-25.2		89

Table II (Continued)

Reference	Source of Sample	Activated Sludge Influent (mg/l^{-1})	Range of Removal Efficiency (%)	Average Removal Efficiency (%)
21	LS	1-10		52
22	LS	33-54.5		90
15	LS	0.15		35
			33-98+	66*
		Iron		
10	ST	1.0-2.95	95-98	97
7	ST	0.457-0.7	87-88	88
7	AT	1.047		72
			72-98	86*
		Lead		
10	ST	0.02-0.05	83-95	89
3	ST	0.01-0.49	42-100	79
12	ST	0.02-0.06	43-63	73
17	ST	0.14-0.4	97-99	65
4	ST	0.16	43	
7	ST	0.98-1.1		53
13	PP	0.055		60
14	PP	0.095		56
20	LS	2.1-25.5		98
15	LS	0.085		17
			27-100+	64*
		Magnesium		
11	PP	8.6-9.8	7-8	8
3	ST	0.02-0.1	25-31	6
7	ST	0.032-0.038		28
14	PP	0.067		25
			6-31+	20*
		Mercury		
10	ST	0.0002-0.0014	92-100	97
3	ST	0.001-0.0009	68-76	62
4	ST	0.0006		17
7	ST	0.0005		72
14	PP	0.00051		69
			17-100+	63
		Nickel		
10	ST	0.06-0.25	40-74	55
3	ST	0.03-1.6	0-100	1
16	ST	0.02-0.04	25-57	61
17	ST	0.05-0.08	28-42	45
7	ST	0.191	53-65	41
13	PP	0.077-0.2		9
6	PP	1		33
2	PP	2.0-10		28
14	PP	0.073		21

Table II (Continued)

Reference	Source of Sample	Activated Sludge Influent (mg/l^{-1})	Range of Removal Efficiency (%)	Average Removal Efficiency (%)
20	LS	2.1		58
15	LS	0.14-25.3		14
			0-100+	33*
10	ST	0.18-0.51	91-97	93
3	ST	0.23-8.94	67-90	50
16	ST	0.31-0.6	44-75	78
17	ST	0.5-0.6	74-96	60
4	ST	0.35	78-100	48
7	ST	0.18-0.43		60
13	PP	0.527		57
5	PP	2.5-20		89
2	PP	9.0		89
14	PP	0.32		65
22	LS	7.5-15		89
15	LS	0.68		49
			44-100+	69*

*Average removal efficiency from all data presented
+Range of removal efficiency from all data presented
Adapted from (9)

most toxic heavy metals to biological treatment processes (2, 23). Barth et al. (2) found that copper exerted a much more inhibitory effect on biological processes than did chromium, zinc or nickel, whether the metals were applied as continuous or slug dosages. McDermott et al. (19) studied the effects of copper on activated sludge processes. It was reported that the effluents of the activated sludge units receiving 10, 15, and 25 mg/l copper fed as copper sulfate were generally of lower quality than those of the control units. They observed that turbidity increased with increasing copper concentrations. The maximum concentration of copper that did not have a detectible effect on BOD and COD of the effluent was 1 mg/l. Copper as copper cyanide complex was also fed at the concentrations of 0.4, 1.3, 2.5, and 10 mg/l as copper. After the systems had acclimated to cyanide, there did not appear to be any difference in the effects of copper when applied as copper sulfate or copper cyanide. They concluded that the activated sludge process was 50-90% efficient in removing copper.

Placak et al. (24) showed that copper had a very deleterious effect on BOD removal. The results indicated that concentrations as low as 0.01 ppm caused detectible reduction in BOD removal, and at 0.05 ppm of copper, BOD removal was decreased by about 23 percent.

Directo et al. (25) studied the effects of copper on the activated sludge process at concentrations of 15, 30, and 45 mg/l. It was concluded that at a given solids concentration and copper ion, the toxic action exhibits an accelerated rate of increase with feed concentration (feed concentrations were 200, 300, and 400 mg/l in terms of COD). They also found that the toxic effects of the copper ion at constant concentration was less at higher solids concentration (solids concentrations

were 2000, 3500, and 5000 mg/l).

Shumate (26) found that the respiratory activity of microorganisms was significantly affected by low copper concentrations. His experiments showed that adding copper continuously to the influent sewage results in a linear decrease in respiratory activity. Dawson (27) reported that copper depressed respiration more than did Ni and Cn-. Barth et al. (2) found that a continuous addition of copper at a concentration of 0.4 mg/l did not increase the effluent COD appreciably, but copper at 1.2 mg/l increased the effluent COD significantly. According to Sierp and Fransemeier (28), copper had a detectible effect by increasing turbidity and decreasing nitrification at one ppm. It had a slight effect on the BOD of the effluent in laboratory-scale activated sludge units.

Gellman (29) showed that one ppm concentration of copper had a noticeable effect on the activated sludge process. He also found that the solubility of copper decreases with increasing pH of solution.

The results of Moulton et al. (21) studies indicated that approximately 80-90% of the copper applied to an activated sludge system can be expected to be removed and retained in the sludge. Apparently the extreme buildup of copper in the systems had little effect on the ability of the sludge to take up and retain copper.

Salotto et al. (30) found that the sludges removed from the unit with high organic loading contained more copper than the one with lower organic loading, and consequently the percent copper removal was higher with the higher organic loading than the lower loading. More copper was lost in the final effluent of the lower organic-loaded unit.

Cadmium

The heavy metal cadmium has been found in many types of industrial wastewaters including metallurgical alloying, ceramics manufacture, and electroplating (31, 32). Of the total industrial cadmium use, 90% is utilized in electroplating, pigments, plastics stabilizers, alloying, and batteries.

Shelley and Sherrard (33) conducted a batch study of the effect of shock load of cadmium as cadmium chloride on microorganims. Their investigations indicated that shock loading batch cultures of activated sludge with cadmium at concentrations below 100 mg/l has no effect on microbial growth yield coefficient and COD removal. Other results revealed that the microbial growth yield coefficient decreased as the concentration of cadmium in the wastewater increased from 100 to 1500 mg/l; microbial growth yield coefficient approached zero at 1500 mg/l and COD removal efficiency decreased 50% at very high cadmium concentrations.

Carter and Cameron (34) reported a decrease in the survival rate of the ciliated protozoan Tetrahymena pyriformis at a cadmium concentration of 1.67 mg/l, but not at 0.84 mg/l. Neufeld (36) studied the effect of heavy metals on flocculation which showed that an additional consequence of cadmium toxicity is poor solid-liquid separation. Cadmium appeared to inhibit proper biomass flocculation, resulting in the production of a floc that would be easily carried over the weirs of a secondary clarifier.

Weber and Sherrard (37) reported that COD removal efficiencies for reactors receiving Cd (11) at concentrations of 5.15 and 9.98 mg/l were

slightly less than those found for the control unit. Increasing concentration of cadmium had little or no effect on the kinetic parameters (Y_{max} - maximum yield coefficient) and (b - decay coefficient). They also concluded that the rate of nitrification decreased as influent cd concentration increased.

The results of Kao et al. (38) indicated that the oxygen uptake rate was not affected by the presence of cadmium at a dosage of 2.0 mg/l. However, it seemed that the oxygen uptake rate increased with cadmium accumulation in the sludge. Their experiments showed that the COD removal efficiency was not affected when the cadmium accumulation in the sludge was less than 17 Cd/MLSS x 10^4 l/gm. However, COD removal efficiencies decreased with cadmium accumulations greater than 17 Cd/MLSS x 10^4 l/gm.

Kaneko (39) reported that the oxygen uptake rate was 292 and 238 mg oxygen per gm per hour when cadmium applied was 0.83 and 4.59 mg/l, respectively. These rates of oxygen uptake seem to be one order of magnitude greater than that of the system without cadmium. It was also reported that the COD removal efficiency was 98.8 and 98.4 percent when the activated sludge received continuously a dose of 0.83 and 4.59 mg/l of cadmium, respectively

Chromium

The heavy metal chromium occurs in aqueous systems as both the trivalent (Cr^{+3}) and the hexavalent (Cr^{+6}) ion. Hexavalent chromium present in industrial wastes are added to cooling water to inhibit corrosion. They are employed in the manufacture of inks, industrial dyes and paint pigments, in chrome tanning, plating and electroplating

operations (41).

Moore et al. (42) in their observations on COD removal showed that hexavalent chromium (Cr^{+6}) had little effect on the removal of organic matter even at the high chromium concentration of 50 mg/l. Chromium was fed as Cr^{+6} at five different concentrations ranging from 0.5 to 50 mg/l. This study also indicated that nitrification was inhibited initially by chromium concentration even at the lowest level, but the nitrifying organisms apparently acclimated to the chromium and proceeded to nitrify after 10 days regardless of the chromium concentration fed to the system.

Jenkins and Hewitt (43) studied the effect of chromium on nitrification. They found that the activated sludge system which was able to oxidize 40-50 mg/l ammonia nitrogen to NO_3^- within twelve hours at 18-19 degrees centigrade failed to produce NO_3^- in twenty hours when subjected to 10 mg/l potassium chromate. However, nitrite (NO_2^-) formed instead.

Stone (44) found that potassium chromate at a concentration of one ppm reduced oxygen uptake by 18 percent. Studies by Dawson and Jenkins (27) indicated that trivalent chromium was more toxic to activated sludge than hexavalent chromium.

At Grand Prairie, Texas, Wells (45) found that poor settling of activated sludge and low treatment efficiency were caused by the presence of chromium in the aeration mixed liquor. Also high dissolved oxygen values were found in the activated sludge. The following conclusions have been made during Bozich's studies (46) upon hexavalent chromium by the activated sludge processes:

1. Nitrification began to be retarded between 0 and 1 ppm concentrations of hexavalent chromium and nitrification was retarded completely

at 4 ppm of hexavalent chromium.

2. The percentage of chromium removed by activated sludge was independent of concentration; 1.5 to 3 percent of the metal fed being removed at concentrations from 1 through 24 ppm.

Moore et al. (42) in their experiments on the effects of chromium on the activated sludge process demonstrated that the amount of chromium in the effluent was negligible when 0.5 mg/l and 2.0 mg/l hexavalent chromium (Cr^{+6}) concentrations were present in the influent. When Cr^{+6} was fed at 20 mg/l it was occasionally found in small quantities in the effluent. Their studies also inferred that accumulation of chromium in the biomass increased as influent concentration of chromium increased.

Mercury (Hg)

Major industrial wastewaters containing mercury are papermills, acetaldehyde production, chemical manufacturing, electrical and electronics industry.

Yamada et al. (47) found that concentrations of $HgCl_2$ as high as 10 mg/l still permitted 90% reduction of the synthetic waste strength when the biomass had been acclimated to mercury. They also reported that at 100 mg/l $HgCl_2$, the uptake of mercury was 96 mg/gm of dry sludge solids. Ghosh and Zugger (48) studied the effect of mercury in the form of $HgCl_2$ at dosages of 1.0, 2.1, 2.4, 5.0, and 10.0 mg/l as Hg^{+2} on a batch-fed system. The results of this investigation indicated that mercury at 1.0, 2.1, and 2.5 mg/l concentrations had no discernible effects on COD removal. However, removal was retarded significantly at dosages of 5.0 and 10.0 mg/l. The results of this study

also indicated that the threshold mercury concentration in batch reactors having MLVSS concentration of 2000 mg/l lies between 2.5 and 5.0 mg/l as Hg^{+2}. They also reported that batch systems can achieve 51 and 58% removal of soluble mercury when 5.0 and 10.0 mg/l mercury, respectively, was added to the system.

Lesperance (49) in a review of the literature reported that mercuric chloride at a concentration of 27 mg/l caused 96% inhibition of respiration.

Neufeld et al. (40) reported that toxic effect of mercury decreased as substrate concentration increased.

Nickel

Wastewaters containing nickel originate from the motor vehicle, aircraft industries, pickling, plating of nickel and nickel alloys. High levels of nickel have also been reported in wastes from silver refineries.

Effects of Nickel on the Activated Sludge Process

McDermott et al. (6) studied nickel and its effects on the activated sludge process. Four different concentrations (1, 2.5, 5 and 10 mg/l) nickel were introduced to the systems. Their investigation indicates that a continuous dosage of 1 mg/l had no significant effect on the treatment efficiency of the activated sludge process. However, there were significant increases in effluent BOD and COD at the 2.5, 5, and 10 mg/l dosages. These results infer that the effects of nickel on the activated sludge system are not linear with concentration, but display decreasing response to increasing concentration. The increased BOD and

COD of the final effluents of the nickel-fed units in comparison to the control units were about the same for dosages of 5 and 10 mg/l.

Slug doses of nickel were also examined at concentrations of 25, 50, and 200 mg/l for four hours by McDermott et al. (6). In each case, the activated sludge was acclimated to a continuous 2.5 mg/l nickel dosage before the slug dose was applied. The slug doses of 25 and 50 mg/l did not seriously upset the system. However, the results for the 200 mg/l slug indicated a significant deterioration in effluent quality but a recovery after approximately 40 hours. It was concluded that nickel ranging from 2.5 to 10 mg/l can be fed continuously to an activated sludge plant with reduced BOD removal efficiencies on the order of five percent. Final effluent was also turbid in comparison with the control unit. The maximum level of nickel which will not produce a detectible effect on treatment efficiencies seemed to be greater than 1 mg/l and less than 2.5 mg/l.

Sujarittanonta et al. (50) found that the COD removal efficiency was not significantly affected with influent nickel concentration as high as 5 mg/l at sludge age values greater than five days. However, it appeared that COD removal efficiency did depend on COD/Ni^{+2}. The values of Y_t (true cell yield) and K_d (decay coefficient) appeared to be dependent on COD/Ni^{+2} in the feed solution. Bozich (46) found that 16.5% removal of nickel is achieved at an influent concentration of 24 ppm. It was also concluded that nitrification was retarded at nickel concentrations of 8 mg/l.

The efficiency of primary and activated sludge treatment for removing nickel has been presented by McDermott et al. (6) and is shown in Table III. It was indicated that approximately 30-35% of the influent

TABLE III

EFFECTS OF NICKEL ON TREATMENT SYSTEMS

	Concentration of Ni in Sewage Feed, $NiSO_4$ (mg/l)							
	0	1	0	2.5	0	5	0	10
Average effluent characteristics								
BOD (mg/l)	21	23	13	26	9	13	9	14
COD (mg/l)	48	51	59	63	40	51	40	54
Suspended Solids (mg/l)	8	11	5	9	8	16	8	17
Turbidity (standard units)	25	34	10	29	4	15	4	28
Efficiency of Ni Removal								
Primary Treatment (%)	5		--		--		3	
Complete Activated Sludge (including primary)	28		42		--		28	

	Concentration of Ni in Sewage Feed, $NiSO_4$ (mg/l)					
	Total ^{10}	Soluble	Total ^{20}	Soluble	Total ^{40}	Soluble
Disposition of Ni in Sludges						
Primary	62	9.8	--	12.8	308	13.2
Excess Activated	89	8.9	--	--	--	--
Digested Primary	44	1.6	--	1.9	--	1.5
Digested Combined (primary plus excess activated)	70	1.6	--	--	--	--

Adapted from (3)

nickel would be removed in the primary and activated sludge systems. Thus, it appears that nickel does not adsorb and will pass through the system in large quantities.

Zinc

Industries discharging waste streams which carry significant quantities of zinc include steelworks with galvanizing lines, zinc and brass metal works, newsprint paper production, silver and stainless steel tableware manufacturing. Zinc salts are also used in the inorganic pigments industry, and high levels of zinc have been reported in acid mine drainage water.

Effects of Zinc on the Activated Sludge Process

McDermott et al. (5) conducted a study of zinc and its effects on the activated sludge process. Three different concentrations (2.5, 10, and 20 mg/l) zinc as zinc sulfate were examined, and in a parallel study, zinc cyanide at a concentration of 10 mg/l was used. Data were taken after the unit had acclimated to the cyanide content of the waste. The data indicated that 2.5 mg/l zinc caused no deleterious effects on the removal efficiency, while 10 mg/l concentrations of zinc (as $ZnSO_4$) tended to show slight increases in effluent BOD, COD, suspended solids, and turbidity. The results showed no significant difference between the effect of two forms of zinc at a dosage of 10 mg/l. It was concluded from their study that the maximum level of zinc in the form of $ZnSO_4$ did not produce deleterious effects on treatment efficiency is greater than 2.5 mg/l and less than 10 mg/l. Stones (51) reported that zinc was removed up to 90% by the activated sludge system.

Removal of Zinc Through the Treatment Facility

McDermott et al. (5) reported that microbial floc of secondary treatment was extremely efficient. The overall process (primary and secondary treatment) is apparently 74-95% efficient in removing zinc at feed levels of 20 and 2.5 mg/l, respectively. This study also showed that zinc concentration in the sludge was increased as the zinc level in the feed increased.

NEUFELD (40) reported that the effect of zinc was constant until a threshold concentration was reached. When metal concentrations increased above the threshold value, the toxicity of zinc was increased. It was also noted that the toxicity of zinc was independent of organic loading.

Lead

Lead is used as an industrial raw material for storage battery manufacture, printing, pigments, fuels, photographic materials, and matches and explosives manufacturing. It is one of the most widely used nonferrous metals in industry (41).

Bozich (46) found that nitrification was retarded at lead concentrations of 8 mg/l. At a lead concentration of 24 ppm in the influent, activated sludge contained nearly 14 percent of the metal by weight. Over 60% of the lead introduced into the influent at a concentration of 24 ppm was found in the waste activated sludge. Stones (52) showed that activated sludge systems removed 90% of the lead in the settled sewage, the remaining 10% passing out with the effluent. Rossin (53) reported that the activated sludge system was able to remove lead up to 82%.

Combined Heavy Metals

In the majority of cases, particularly combined municipal treatment facilities, the concern of heavy metals is not related to one or two metals, but to a mixture or combination of heavy metals originating from one or several industrial sources.

Effects of Combined Heavy Metals on the Activated Sludge Process

A study on the effects of a mixture of heavy metals on sewage treatment processes was conducted by Barth et al. (54). This study was conducted on a pilot scale with the heavy metal concentrations shown in Table IV. The average characteristics of the final effluents from these systems are shown in Table V. These data showed that MC#1 and MC#2 had a significant effect on the performance of the system in terms of COD, while the effects of MC#3 combinations were very marginal.

TABLE IV

METAL COMBINATIONS FED TO ACTIVATED SLUDGE PROCESSES

Metal Combination	Metal (mg/l) Influent Sewage				Total Heavy Metals (mg/l)	Totat CN
	Cu	Cr	Ni	Zn		
MC#1	0.4	4.0	2.0	2.5	8.9	4.3
MC#2	0.4	-	2.0	2.5	4.9	4.3
MC#3	0.3	-	0.5	1.2	2.0	2.0

Adapted from (54)

TABLE V

EFFLUENT QUALITY FROM CONTROL AND METAL-FED UNITS

Metal Combination Fed	BOD	COD	Suspended Solids (mg/l)	Standard Turbidity Units
MC#1	27	66	15	39
Control	18	45	10	26
MC#2	21	63	16	74
Control	21	48	13	32
MC#3	16	57	9	22
Control	21	52	12	16

Adapted from (54)

This study concluded that combined heavy metals did not exert synergistic effects on the activated sludge process and that the combined effect was no more severe than the effect that one metal alone would have at the same concentration. The results indicated that the removal efficiency was highest for zinc at 90% and lowest for nickel at 31% for the activated sludge system.

Factors Affecting Metal Removal in Activated Sludge

Many different factors have been shown to affect the removal of heavy metals in the activated sludge process (9). These may be divided into plant operating parameters, physical or chemical factors and biological factors. Operating parameters which have been shown to affect heavy metal removal are sludge volume index (SVI), sludge age, dissolved oxygen concentration, substrate concentration, and settling time. Physical and chemical factors affecting metal removal are

temperature, pH, metal ion concentration, metal solubility, metal valency, and concentration of complexing agents. The main biological factor is the concentration of bacterial extracellular polymers.

Rudolfs and Zuber (22) found that as SVI increased in activated sludge, the removal capacity for metal decreased. The findings of Stoveland (55) showed that higher heavy metal removal occurred at higher sludge ages, particularly for lead and zinc. Rossin et al. (53) conducted a study of the influence of sludge age on the removal of heavy metals in the activated sludge. Heavy metal removal efficiencies were determined at two different feed concentrations for each metal. Removal for both concentrations are shown in Table VI. As can be seen, the removal of Ni was appreciably poor (ranging between 11 and 36%), while the removals of Cu and Pb were generally good. The removals of Cd, Cr, and Zn varied between 8 and 80%, 10 and 68%, and 70 and 84%, respectively.

TABLE VI

HEAVY METAL REMOVAL EFFICIENCY (%R) FROM SPIKED SETTLED SEWAGE AT SLUDGE AGES OF 4, 9, and 12 DAYS

Θ_c	Cd		Cr		Cu		Ni		Pb		Zn	
Day	Conc µg/l	%R	Conc µg/l	%R	Conc µg/l	%R	Conc µg/l	%R	Conc µg/l	%R	Conc µg/l	%R
4	0.43	68	42.0	10	46.4	81	21.0	11	16.6	66	88	41
9	1.40	33	5.6	55	56.2	70	17.6	36	24.0	80	156	51
12	2.98	8	5.8	49	65.9	74	20.8	22	29.3	32	127	39
4	7.13	60	112	46	176	83	173	16	56.3	69	545	55
9	12.2	80	80	62	137	82	119	16	64.3	77	576	68
12	8.4	60	35.6	68	138	84	94.7	33	66.2	82	675	40

Adapted from (53)

The accumulation of heavy metals by the mixed liquor under steady state conditions at each sludge age was determined. The data showed that the accumulation of Cd by the mixed liquor decreased with increasing sludge age (4, 9, and 12 days) at low metal dosage. The greatest uptake of Cr, Cu, Ni, and Pb occurred at 9-day sludge age when they were added at lower dosage. However, the greatest uptake of Cr, Cu, Ni, and Pb occurred at 12-day sludge age when metals were added at higher concentration. The highest accumulation of zinc occurred at 12-day sludge age under low and high metal loadings.

Sterritt and Lester (56) operated the activated sludge at six different sludge ages (3, 6, 9, 12, 15, and 18 days) to show the influence of sludge age on heavy metal removal in the activated sludge process. Ten different heavy metals were examined. The removal efficiencies of Cu, Ni, Ag, and Zinc decreased as sludge age increased from three to nine days and then increased to maximum removal of Cu, Ag, and Zinc at 15 day and Ni at the 18 day. They concluded that Cd and Cr were removed with efficiencies of 50% or more. The removals of cobalt, manganese, molybdenum and nickel were poor. It was also shown that the removal of cobalt, manganese, and molybdenum were independent of changes in the sludge age. Their investigation also indicated that the highest removal efficiencies for metals occurred at the 15-day Θ_c except for Ni and Pb. The removal of Cr was highest (95%) among the metals.

Mechanism of Heavy Metal Uptake in the Activated Sludge Process

Several possible mechanisms of metal removal in activated sludge have been proposed (9). These mechanisms are:

1. Physical trapping of precipitated metals in the sludge floc matrix;
2. Binding soluble metal to extracellular polymers;
3. Accumulation of soluble metal by the cell.

The uptake of the heavy metals in the activated sludge process was investigated by several authors (20, 40, 57). Chenge et al. (20) in his studies indicated that the uptake of heavy metal by activated sludge can be characterized by a short-term rapid metal uptake phase followed by a long-term, slow phase uptake. Neufeld et al. (40) conducted laboratory studies with batch cultures of activated sludge which were acclimated to heavy metals. They concluded that the affinity for metals by sludge decreased in the order of Hg>Cd>Zn. Their experiments showed that all concentrations which were used for Hg, Cd, and Zn there was a rapid uptake by the sludge and followed by a slow uptake.

Parsons and Dugan (58) reported that microorganisms excreted extracellular polysaccharides which have a certain affinity for various heavy metals. Heavy metals present could bind to these polymers. Dugan et al. (59) reported that pure cultures of Zoogloea remigera, a typical activated sludge organism, consists of a highly polymerized extracellular polymer.

Friedman and Dugan (60) compared the uptake of metal ions by two strains of Z. ramigera: Z. ramigera 115, an extensive polymer producer forming zooglocae, and Z. ramigera 1-16-M, which produced no zoogloeal matrix. They found that Z. ramigera 1-16-M accumulated only half as much metal as Z. ramigera 115. They therefore suggested that the zoogloeal matrix may be responsible for half the metal uptake by zoogloeal cell flocs and that total metal uptake is determined by the

combined influence of the cell and the zoogloeal matrix.

Bitton and Freihofer (61) have investigated the influence of bacterial extracellular polysaccharides on copper and cadmium toxicity to two strains of K. aerogenes, one capsulated strain and one non-capsulated strain. They found that the capsular polysaccharide acted as a protective mechanism against copper toxicity and to a lesser extent, cadmium toxicity. Extracellular polymers consistently complexed copper more than cadmium. This would explain the difference in the protective ability observed. They concluded that the toxicity of a metal doese to bacteria was reduced by complexation with extracellular polymers.

CHAPTER III

MATERIALS AND METHODS

To accomplish the goal of studying the fate of selected heavy metals and their effect on the activated sludge, a number of completely mixed continuous flow reactors were employed.

Three heavy metals used in this investigation were cadmium as cadmium acetate ($Cd(C_2H_3O_2)_2 \cdot 2H_2O$), lead as lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$), and zinc as zinc acetate ($Zn(C_2H_3O_2)_2 \cdot 2H_2O$).

Laboratory Apparatus

A diagram of the bench scale activated sludge used in this investigation is shown in Figure 1. The plexiglass reactors with internal recycle system were used. The aeration and settling compartments were separated by an adjustable plexiglass baffle. The total volumes of the reactors were 4.70, 4.70, 4.90, and 4.72 liters. The volumes of aeration tanks and clarifiers were 3.00, 2.74, 2.90, and 3.05, and 1.70, 1.97, 2.00, and 1.67 liters, respectively. Air was supplied to the aeration compartment through two sintered glass diffusers at an average rate of 3.0 liters per minute to provide an adequate oxygen supply to the biomass as well as to keep the solids in the aeration tank completely mixed. A pump was used to provide a continuous flow to the system.

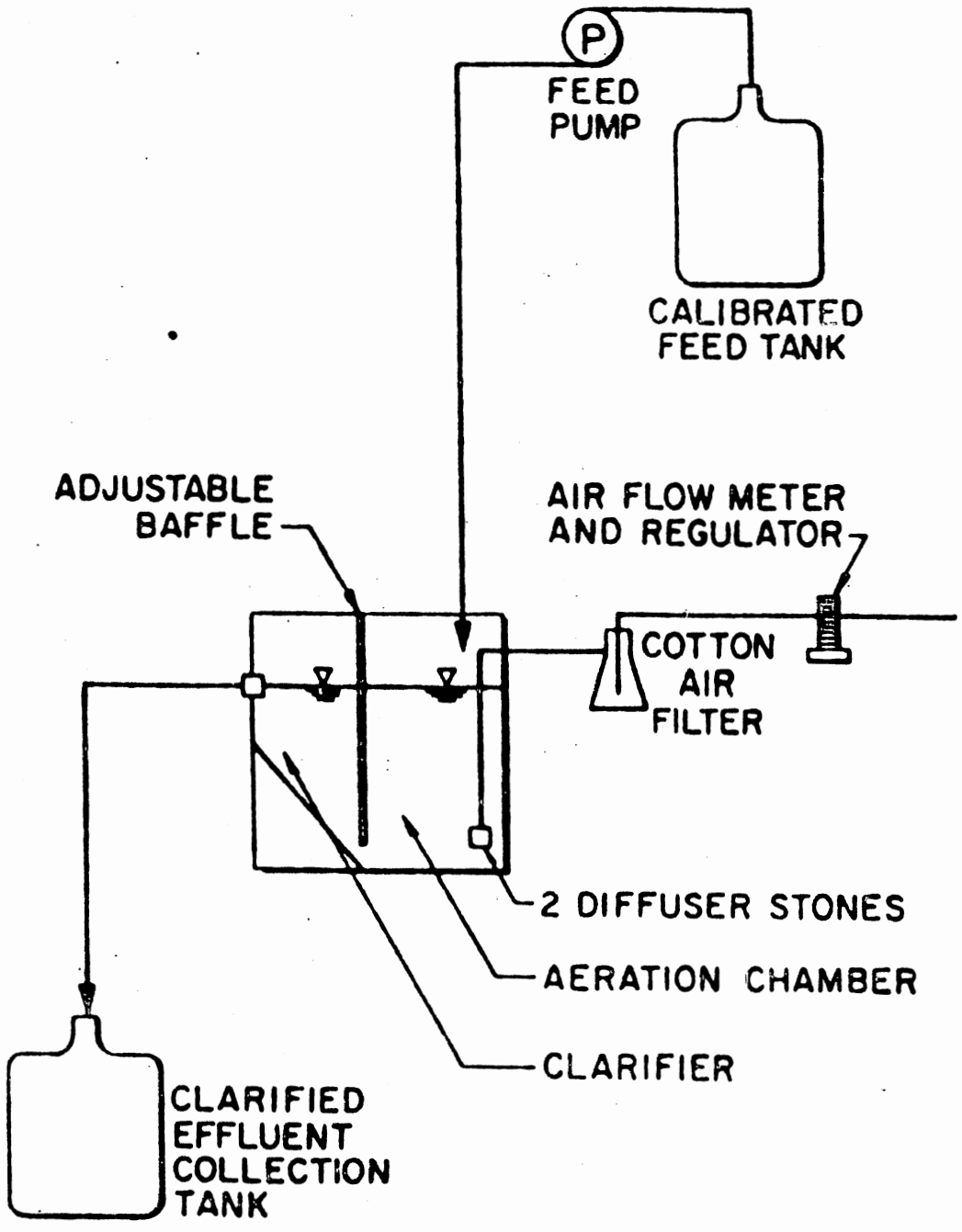

Figure 1. Experimental Activated Sludge Unit with Internal Recycle

Initial Startup

The original seed of microorganisms for these experiments was obtained from the municipal sewage treatment plant in Tulsa, Oklahoma. These microorganisms were acclimated to the synthetic feed solution by being fed continuously in a continuous flow system.

System Operation

The laboratory-scale completely mixed activated sludge systems were operated at a hydraulic detention time of 10 hours over a wide range of process conditions (solids retention time, SRT) and different influent heavy metal concentrations. Prior to the addition of heavy metals with the exception of cadmium, the systems were operated at steady state for a period of four to eight weeks with a synthetic wastewater. This period was used as the control. For the cadmium study at three and 20-day SRT, the control systems were operated in parallel to the units which received cadmium. Sludge was wasted daily after removing the baffle to achieve desired solids retention time (SRT). The volume of sludge wasted was determined by using the aeration tank volume.

Synthetic Wastewater

The constituents of the complex wastewater included "Sego," ammonium chloride and phosphate buffer. The ingredients of "Sego" supply a carbon source, protein, vitamins, and a balance of chemical elements. The ingredients listed on the "Sego" label included concentrated skimmed milk, sugar, vegetable oils, edible cellulose, magnesium sulfate, artificial flavor, salt, cellulose gum, magnesium oxide, sodium

ascorbate (Vitamin C), ferric orthophosphate, carrageenan, atocopherylacetate (Vitamin E), niacinamide, zinc oxide, copper gluconate, calcium pantothenate, Vitamin A palmitate, pyridoxine hydrochloride (Vitamin B_6), riboflavin phosphate (Vitamin B_2) thiaminhydrochloride (Vitamin B_1), folic acid, biotin, potassium iodide, Vitamin D_3, and Vitamin B_{12}.

According to the nutritional information given by the manufacturer, a ten-ounce (295.7 ml) can of "Sego" contains 11 grams of protein, 34 grams of carbohydrate, and five grams of fat.

A volume of 2.7 ml of "Sego" was dissolved in one liter of tap water to form the complex wastewater which produced 400-600 mg/l COD and 180-220 mg/l TOC.

In addition to 2.7 ml/l of "Sego" as carbon source, 7.2 mg of nitrogen as NH_4Cl, 211.2 mg of potassium phosphate monobasic (KH_2PO_4) and 53 mg of KOH were added to one liter of tap water. In addition to NH_4Cl feed solution contained 110 mg/l protein, which was accounted for the nitrogen source. The last two compunds provided enough nutrient potassium hydroxide, and KH_2PO_4 and KOH maintained the pH of the system at a range of 7.1 to 7.4.

Analytical Technique

The analytical tests performed during this study were chemical oxygen demands (COD), total organic carbon (TOC), Atomic Absorption Spectrophotometary (AA) dissolved oxygen uptake rate, sludge volume index (SVI), zone settling velocity (ZSV), Capillary Suction Time (CST), suspended solids (SS), pH, and temperature are summarized in Table VII. A diagram of apparatus for measuring the capillary suction

TABLE VII

ANALYTICAL TECHNIQUES USED IN THESE INVESTIGATIONS

Type of Test	Frequency	Method	Source
Suspended Solids (SS)	daily	Glass fiber 934-AH	Standard (62) Methods
COD	three times/wk	Chromic Acid Oxidation	Standard (62) Methods
TOC	three times/wk	Beckman Model 915 TOC Analyzer	Beckman Instruments
pH	three times/wk	Orion Research Model 701 pH Meter	
Dissolved Oxygen Uptake Rate	weekly	Orion Research Model Probe; reduction of oxygen concentration monitored with time	
Heavy Metal	three times/wk	Perkin-Elmer Model 5000 atomic adsorption spectrophotometer (AA)	Instrument
Sample Digestion	three times/wk	Heated nitric acid digestion process	(63)
SVI	weekly	Sludge volume index is the volume in ml occupied by one gram of activated sludge after settling the aerated liquor for 30 min.	Standard (62) Methods
ZSV	weekly	One liter mixed liquor sample was placed in one liter glass graduated cylinders (not stirred) and allowed to settle. Solid supernatant interfer height was recorded vs time	
CST	weekly	Capillary suction time apparatus	(64)

time is presented in Figure 2.

Data Analysis

As was previously mentioned, solids retention time (SRT) was used as a control parameter. Solids retention time was determined using the relationship (65):

$$SRT = \frac{VX}{F_w X_r} + (F - F_w)X_e \qquad (1)$$

The sludge waste flowrate was calculated by rearranging equation (1) as follows:

$$F_w = \frac{\frac{VX}{SRT} - FXe}{X - X_e} \qquad (2)$$

in which

SRT = solids retention time (day)

V = volume of reactor (liter)

F = influent flow rate (liter/day)

X_e = effluent suspended solids (mg/l)

X = aeration tank solids (mg/l)

X_r = waste solids concentration (mg/l)

F_w = waste sludge flow rate (l/day)

COD removal efficiency was determined according to the expression:

$$E = \frac{(Si - Se) \times 100}{Si}$$

where

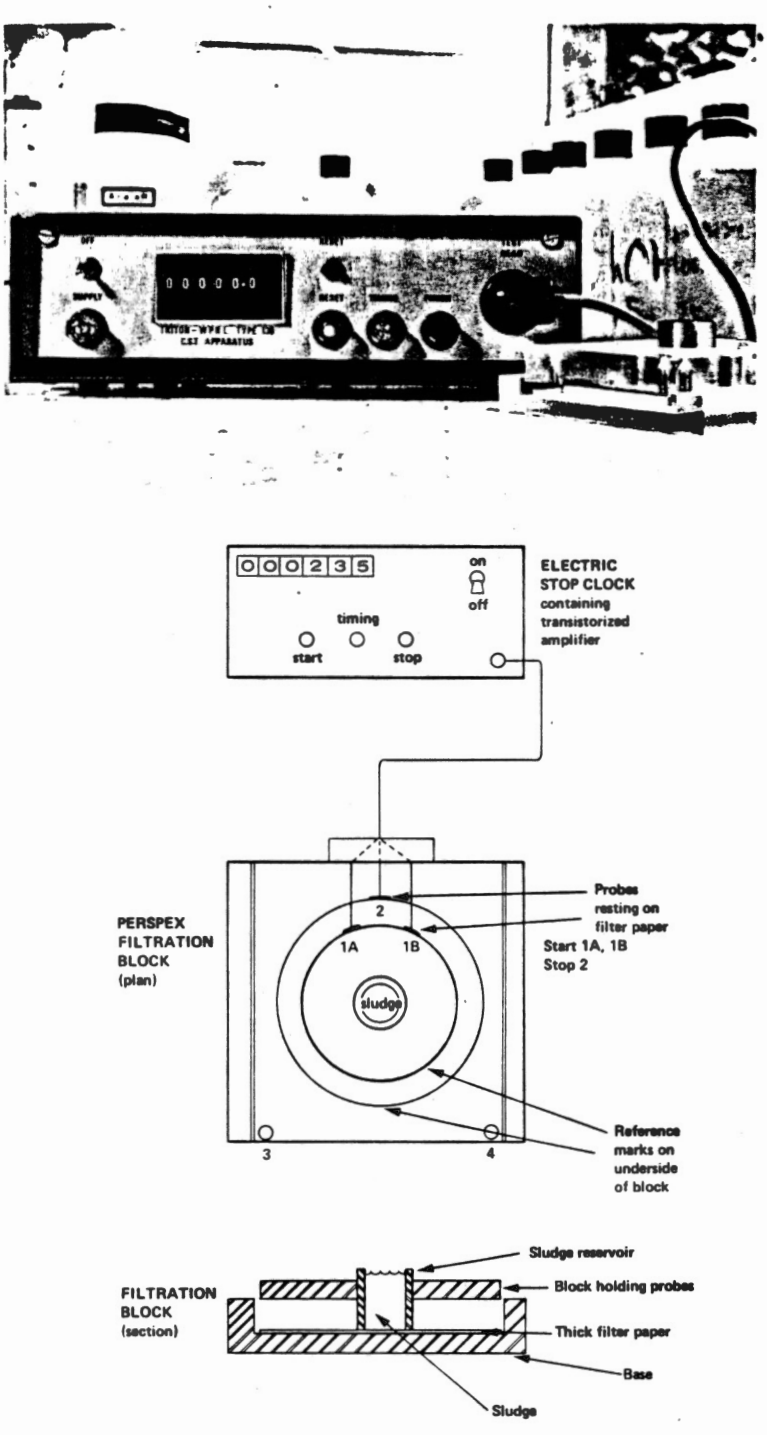

Figure 2. Apparatus for Measuring Capillary Suction Time

E = COD removal efficiency (percent)

Si = influent COD concentration (mg/l)

Se = effluent COD concentration (mg/l)

The value of microorganism cell yielt, Y_t, and maintence energy coefficient, kd, were determined by using equation (65):

$$\frac{1}{SRT} = Y_t U - kd \tag{3}$$

where

SRT = solids retention time

U = specific substrate utilization rate, time - 1

Y_t = microorganism cell yield, mass/mass

kd = maintenance energy coefficient, time - 1

The data obtained from these activated sludge units were analyzed to provide performance information, fate of selected heavy metals, and bio-kinetic constants by the Kincannon and Stover, Lawrence and McCarty, and modified Eckenfelder models.

Mathematical description of the substrate utilization rate (ds/dt)g in the Kincannon and Stover model (66, 67) based on monomolecular kinetics with (ds/dt)g expressed as a function of the mass loading rate or F/M ratio, as follows:

$$\left(\frac{ds}{dt}\right) g = \frac{U_{max} \frac{FSi}{XV}}{k_B + \frac{FSi}{XV}} \tag{4}$$

where

F = flow rate

Si = influent substrate concentration

X = mixed liquor solids concentration

V = reactor volume

U_{max} = Kincannon and Stover's maximum substrate utilization rate

k_B = substrate loading at which the rate of substrate utilization is one-half the maximum rate

U_{max} and k_B can be determined by rearranging equation (4) as follows:

$$\frac{1}{(ds/dt)g} = \frac{k_B}{U_{max}} \frac{1}{\frac{FSi}{XV}} + \frac{1}{U_{max}} \tag{5}$$

Equation (5) represents a linear relationship between substrate utilization rate, U, and mass substrate loading.

To find the biokinetic constant (k_e') based on the Eckenfelder modified design model (65), a material balance for a complete mix continuous flow activated sludge process can be made to describe the rate of change of substrate concentration in the reactor. Mathematical description of the substrate utilization rate will be as follows:

$$U = \frac{k_e' S_e}{S_i} \tag{6}$$

k_e can be calculated by rearranging Equation (6) as follows:

$$S_i U = k_e' S_e \tag{7}$$

The slope of the above equation will be k_e'.

The rate of substrate utilization in the Lawrence and McCarty (65) design model is expressed as follows:

$$\left(\frac{ds}{dt}\right)g = \frac{k \times S_e}{k_s + S_e} \tag{8}$$

where

k = maximum rate of waste utilization

k_s = waste concentration at which the rate of waste utilization is one-half the maximum rate

k and k_s can be determined by rearranging Equation (8) as follows:

$$\frac{1}{\left(\frac{ds}{dt}\right)_g} = \left(\frac{k_s}{k}\right) \frac{1}{S_e} + \frac{1}{k} \qquad (9)$$

The fate of various concentrations of three heavy metals (Cd, Pb, Zn) was studied under three different SRTs. Cadmium was fed continuously at various concentrations such as 4.06, 6.02, 9.67, and 21.60 mg/l at three-day SRT and at concentrations of 4.14, 6.60, 9.20 and 17.28 at 20-day SRT. Cadmium was also fed at concentrations of 1.27, 4.27, and 6.36 mg/l at SRT of six days. Solids retention times were 3, 6, and 12 day for lead and zinc. Lead acetate was introduced to the synthetic waste at four different concentrations such as 0.56, 3.32, 5.46, and 18.08 for three day SRT, and 0.57, 3.65, 6.73, and 19.26 mg/l for 12 day SRT. Six day SRT received only 0.44 mg/l lead. Zinc acetate was fed continuously to the system at 1.14, 4.43, and 9.42 mg/l concentrations at three day SRT, and 1.03, 3.96, 8.29, 20.17 and 37.63 mg/l at 12 day SRT. A system which was operated at six day SRT received 1.83 mg/l zinc continuously.

A laboratory pilot unit which received no heavy metal was run at 3, 6, 12, and 20 day SRT as a control system. The data collected from the systems receiving each heavy metal individually and in combination were compared with the data gathered from the control system.

CHAPTER IV

RESULTS

Performance of Activated Sludge Control Systems

In order to assess the impact of heavy metals upon the performance of the activated sludge systems, it was necessary to collect background data on systems not exposed to heavy metals. Therefore,four control units were operated at different solids retention times (3, 6, 12, and 20 day).

The performance of the control units at 3, 6, 12, and 20 day SRTs are presented in Figures 3 through 6, respectively.

Figure 3 shows the operational data of the 3 day SRT reactor. It can be seen that the reactor was maintained at a constant solids retention time (SRT) of three days. The influent TOC varied between 155 and 215 mg/l, while influent COD ranged between 380 and 650 mg/l. Mixed liquor suspended solids (MLSS) concentrations ranged between 1600 and 2100 mg/l (average 1750 mg/l). Effluent suspended solids concentrations were fairly low averaging 19 mg/l except for a few days which exceeded 50 mg/l. Effluent soluble TOC concentration averaged 20 mg/l, fluctuating between 12 and 32 mg/l. Effluent soluble COD concentrations varied between 30 and 90 mg/l with an average of 48 mg/l.

The performance of the control unit operated at an SRT of six days and is shown in Figure 4. It can be observed that the system operated at

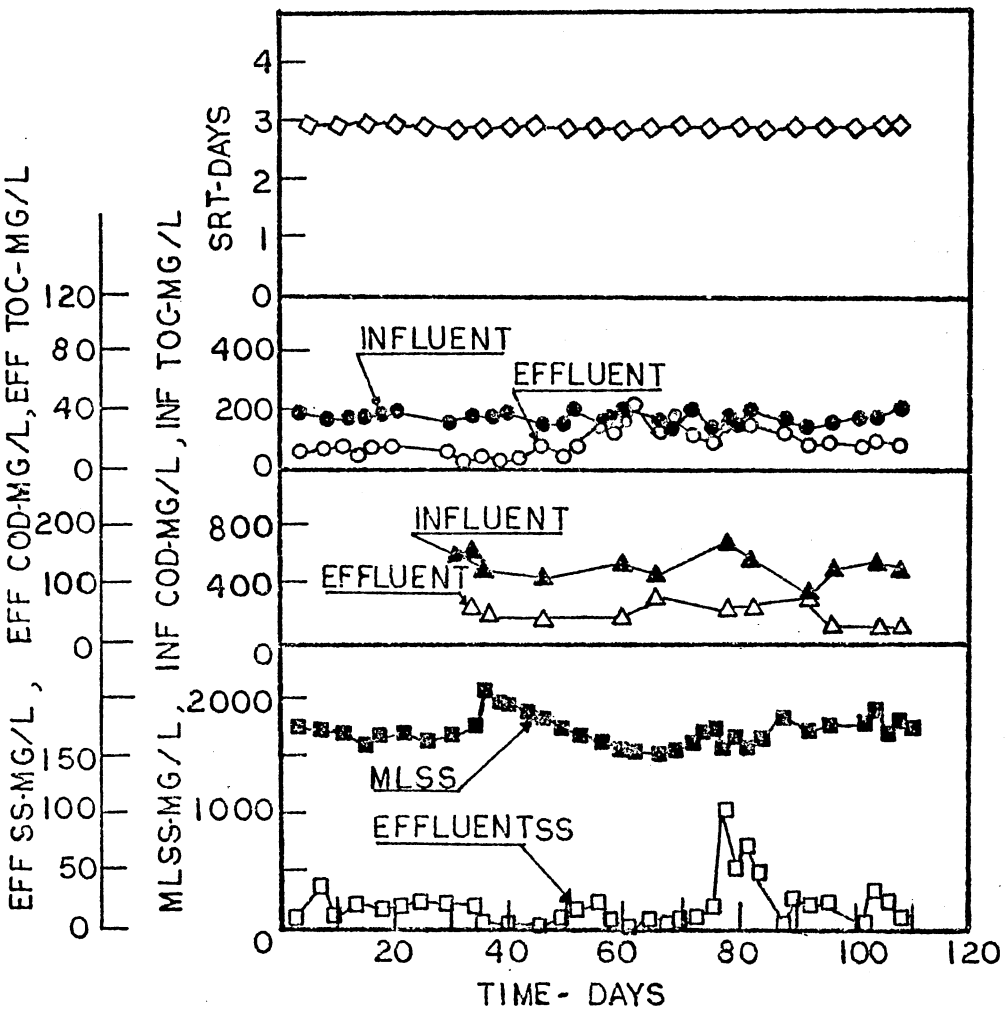

Figure 3. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 3 Days Receiving a Wastewater Composed of No Metal

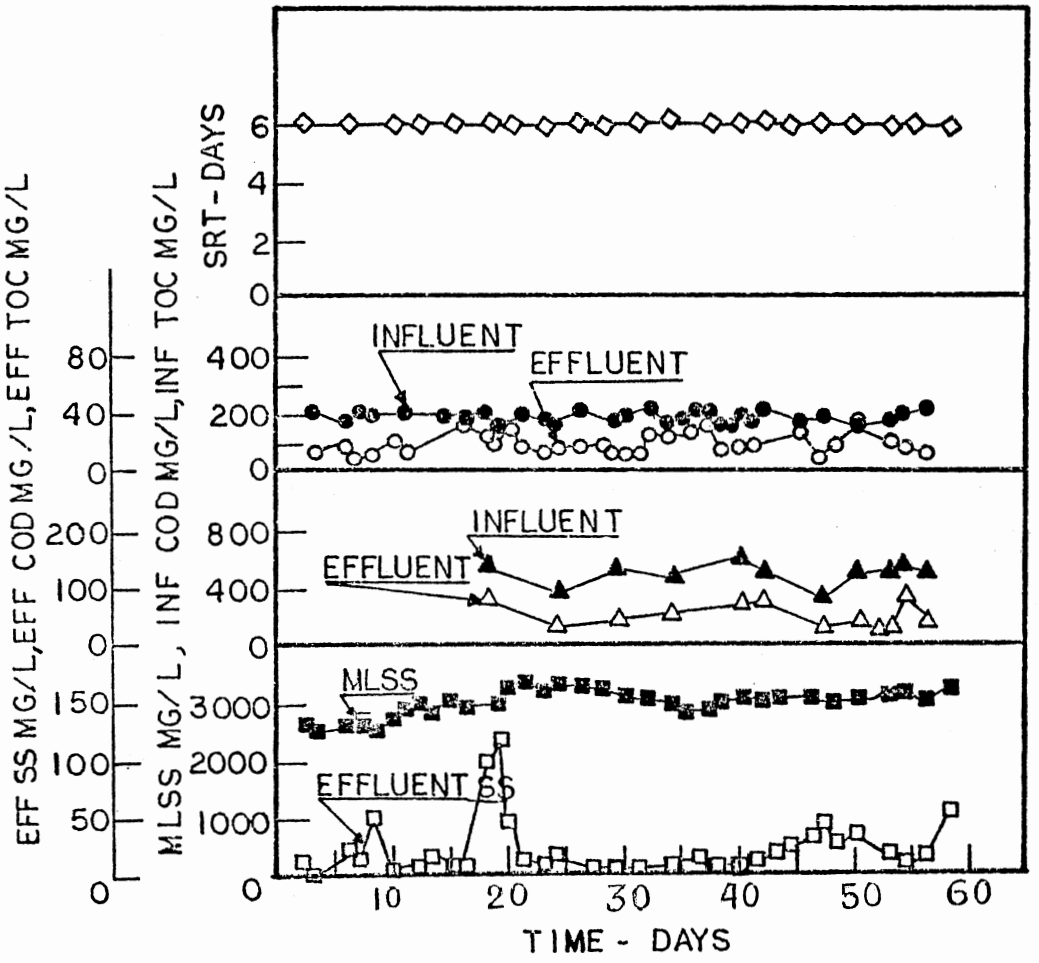

Figure 4. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 6 Days Receiving a Wastewater Composed of No Metal

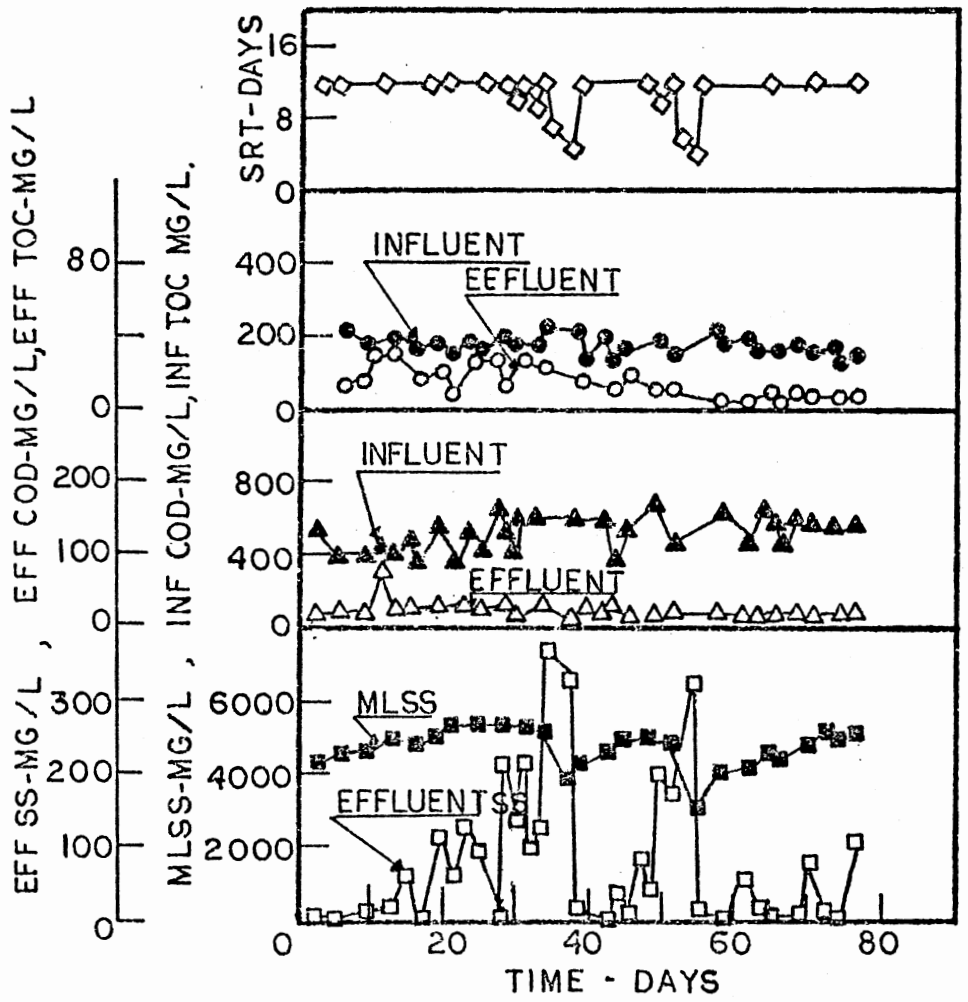

Figure 5. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 12 Days Receiving a Wastewater Composed of No Metal

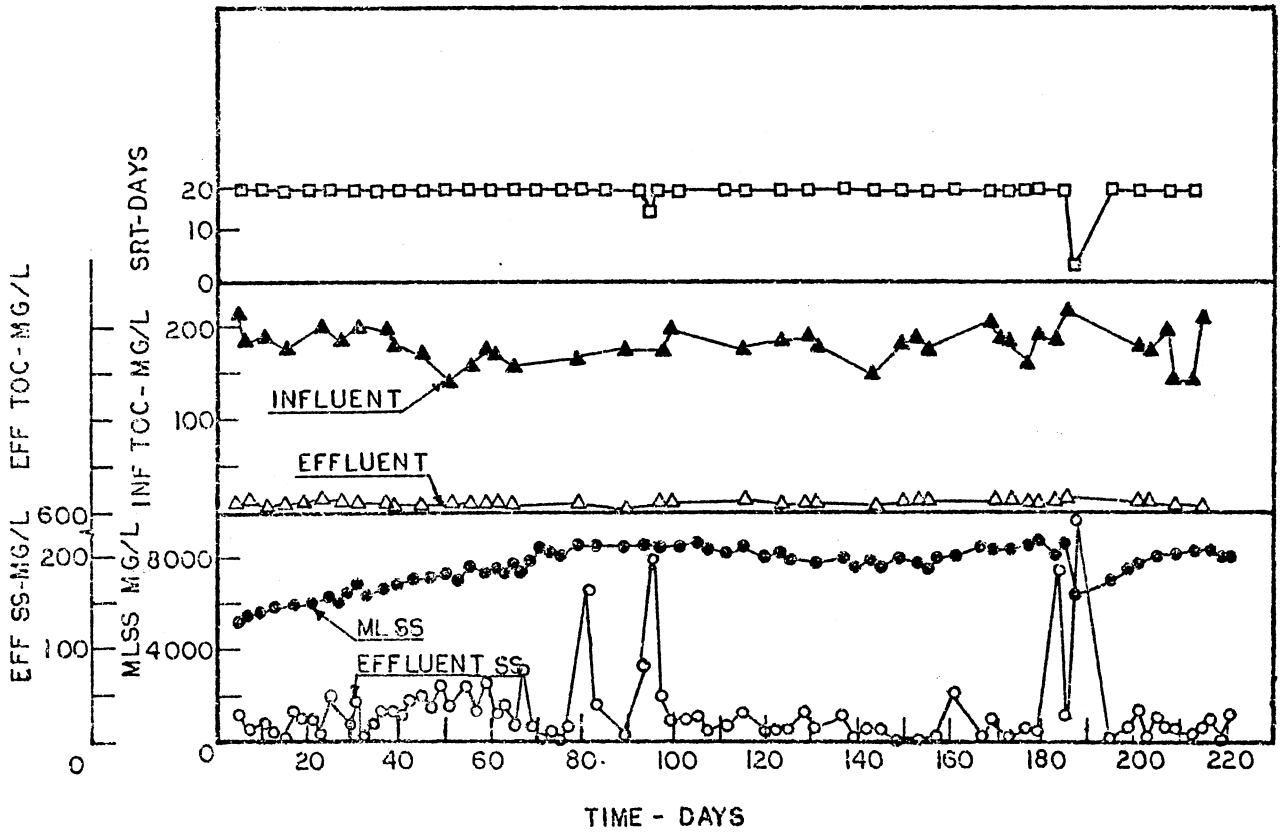

Figure 6. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 20 Days Receiving a Wastewater Composed of No Metal

a fairly good steady state. The influent TOC varied between 150 mg/l and 220 mg/l, with an average of 182 mg/l, while the influent COD ranged between 320 mg/l and 600 mg/l. The mixed liquor suspended solids concentration fluctuated within a range of 2500 mg/l and 3400 mg/l with an average of 3100 mg/l. The system was efficient in removing influent substrate in terms of COD and TOC (90% removal efficiency). The effluent TOC varied between 8 and 36 mg/l with an average of 20 mg/l. The effluent soluble COD was within a range of 30 mg/l and 80 mg/l with an average of 51 mg/l. The effluent suspended solids concentration was generally below 50 mg/l. There was one period of time when the effluent suspended solids concentration exceeded 50 mg/l.

The operating characteristics of the 12 day SRT reactor are presented in Figure 5. As can be seen, it was difficult to maintain the SRT at 12 days. Twice during this run, for a short duration the SRT could not be maintained constant due to the high level of solids in the effluent. Influent TOC varied between 150 and 230 mg/l with an average of 194 mg/l. Influent COD ranged between 360 mg/l and 650 mg/l with an average of 508 mg/l. MLSS concentrations varied between 3200 mg/l and 5400 mg/l with an average of 4700 mg/l. Effluent suspended solids concentrations were generally below 200 mg/l except during the time in which the SRT could not be maintained accurately and exceeded 300 mg/l. Effluent soluble COD was fairly low (less than 30 mg/l) with an average of 22 mg/l. Effluent soluble TOC ranged between 5 mg/l and 30 mg/l with an average of 13 mg/l. The system was able to remove 95.7% of applied COD and 93.3% TOC.

The response of the system which received wastewater containing no metal and operated at an SRT of 20 days can be found in Figure 6. The

system took five weeks to reach a steady state condition with respect to the mixed liquor suspended solids concentration. It can be seen that the reactor was maintained at a constant SRT of 20 days. The MLSS concentration varied around 8200 mg/l at steady state. On day 187, the baffle was kept high accidentally during that night and it pushed the solids out of the reactor, causing the loss of biomass. This resulted in a lower SRT for that day. Effluent suspended solids concentrations fluctuated between 0 mg/l and 95 mg/l with an average of 37 mg/l except for a few occasions when the effluent suspended solids exceeded 150 mg/l. Effluent soluble TOC ranged between 5 and 17 mg/l with an average of 10 mg/l.

Effluent characteristics in terms of COD, TOC, suspended solids and percent removal efficiency for the control systems are shown in Table VIII. Influent soluble COD and TOC are within the range of 482 and 522, and 178 and 194 mg/l, respectively. The treatment efficiencies with respect to COD and TOC are within the range of 90 to 96.3% and 89 to 94.4%, respectively. It can also be seen that the removal efficiencies were the greatest at the highest SRT. The average effluent suspended solids were fairly low (less than 74 mg/l) at all four solids retention times.

Performance of Activated Sludge Systems Receiving Wastewater Containing Lead

The performance of the units exposed to various concentrations of lead are shown in Figures 7 to 9.

Figure 7 represents an activated sludge system operated at an SRT of three days with various influent lead dosages. After 28 days of operation, which is shown as day 5 on Figure 7, 0.56 mg/l Pb was added to the system.

TABLE VIII

EFFLUENT CHARACTERISTICS OF THE CONTROL UNITS

	SRT (day)			
	3	6	12	20
Influent (mg/l)				
Soluble COD	522	509	508	482
Soluble TOC	183	182	194	178
Effluent (mg/l)				
Soluble COD	48	51	22	18
Soluble TOC	20	20	13	10
COD Removal Efficiency (%)	90.8	90.0	95.7	96.3
TOC Removal Efficiency (%)	89.1	89.0	93.3	94.4
SS (mg/l)	19	18	74	37

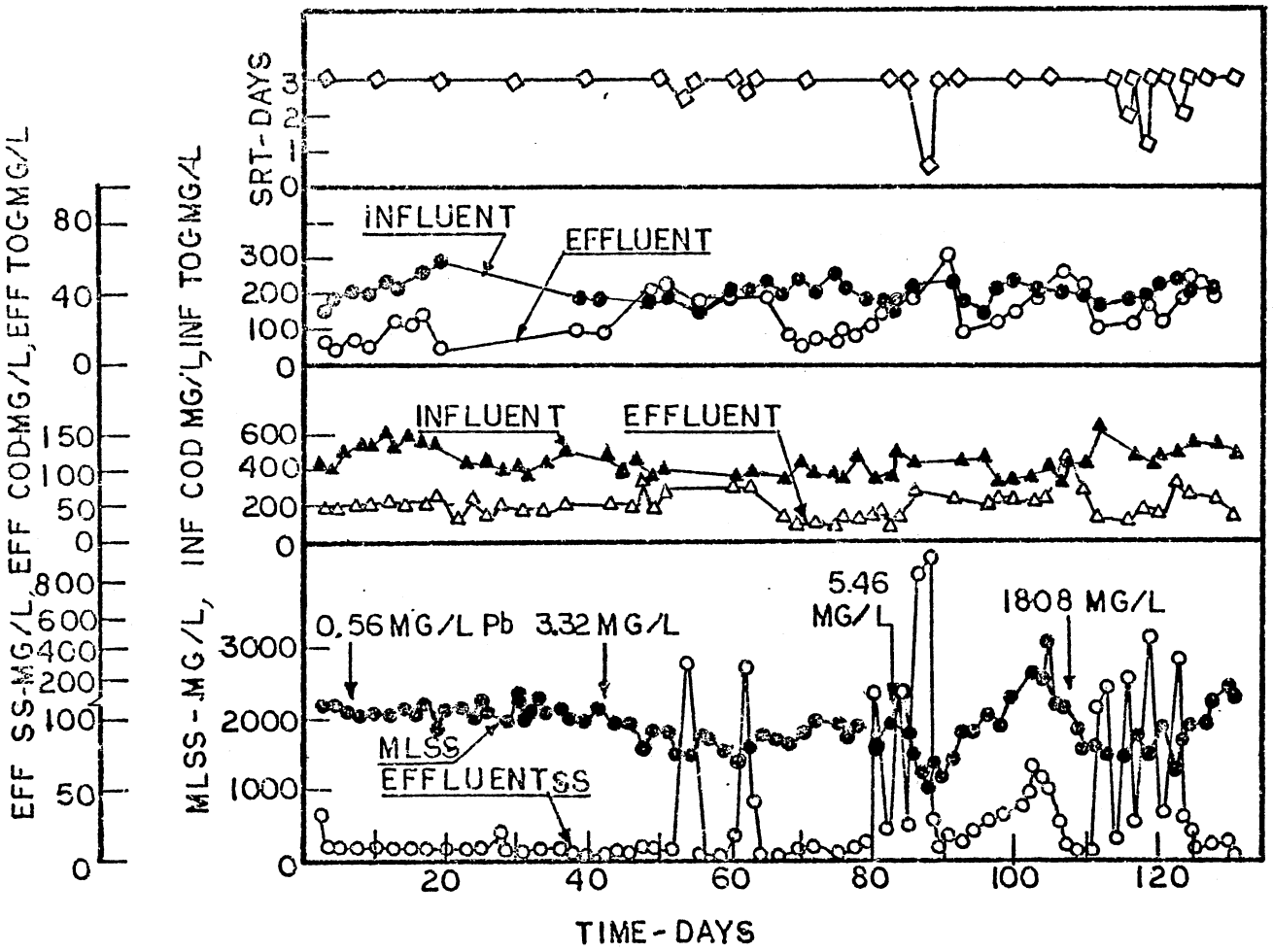

Figure 7. Performance Data for an Activated Sludge Reactor Maintaining at An SRT = 3 Days Receiving a Wastewater Composed of Various Dosages of Lead

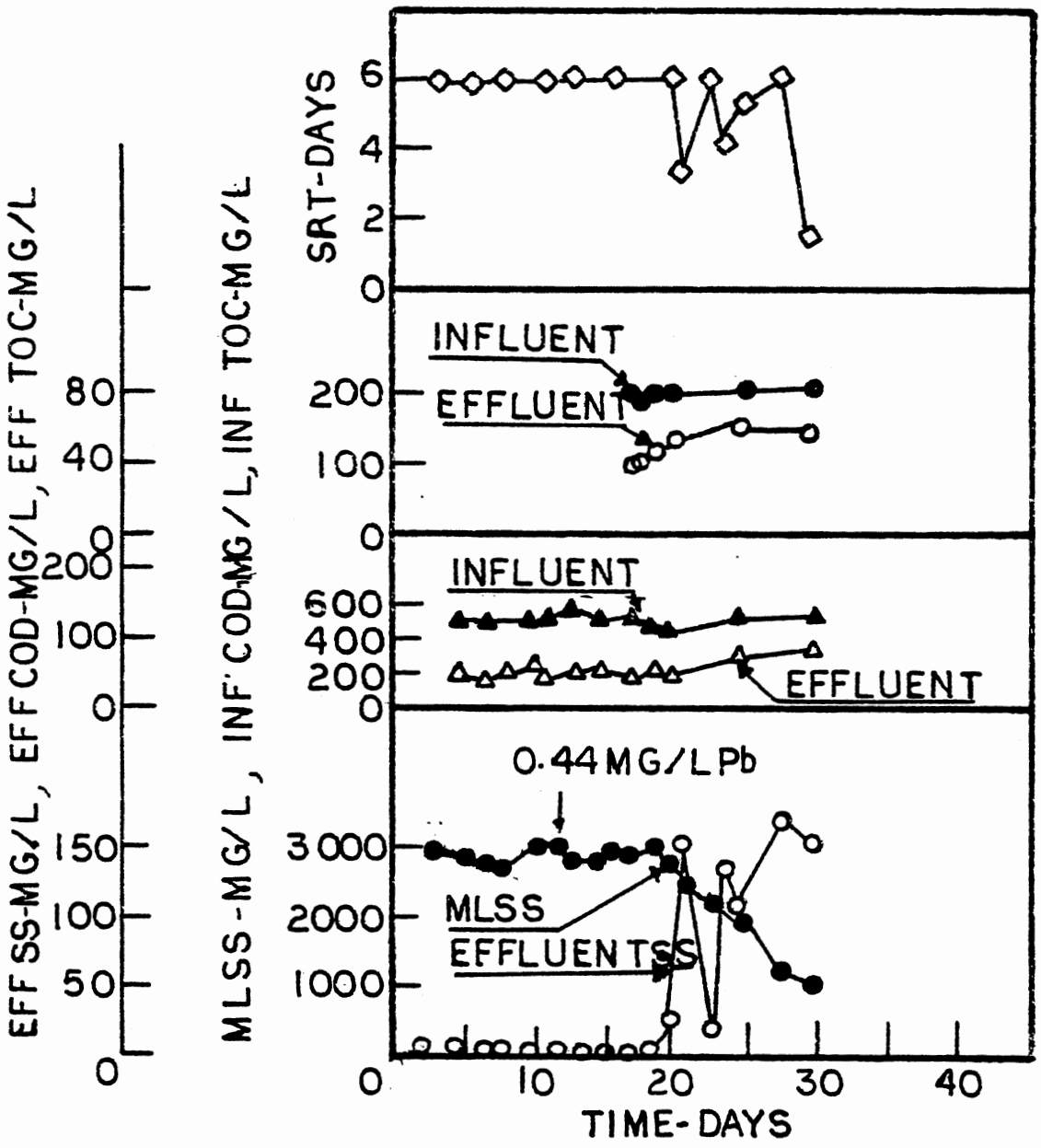

Figure 8. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 6 Days Receiving a Wastewater Composed of Various Dosages of Lead

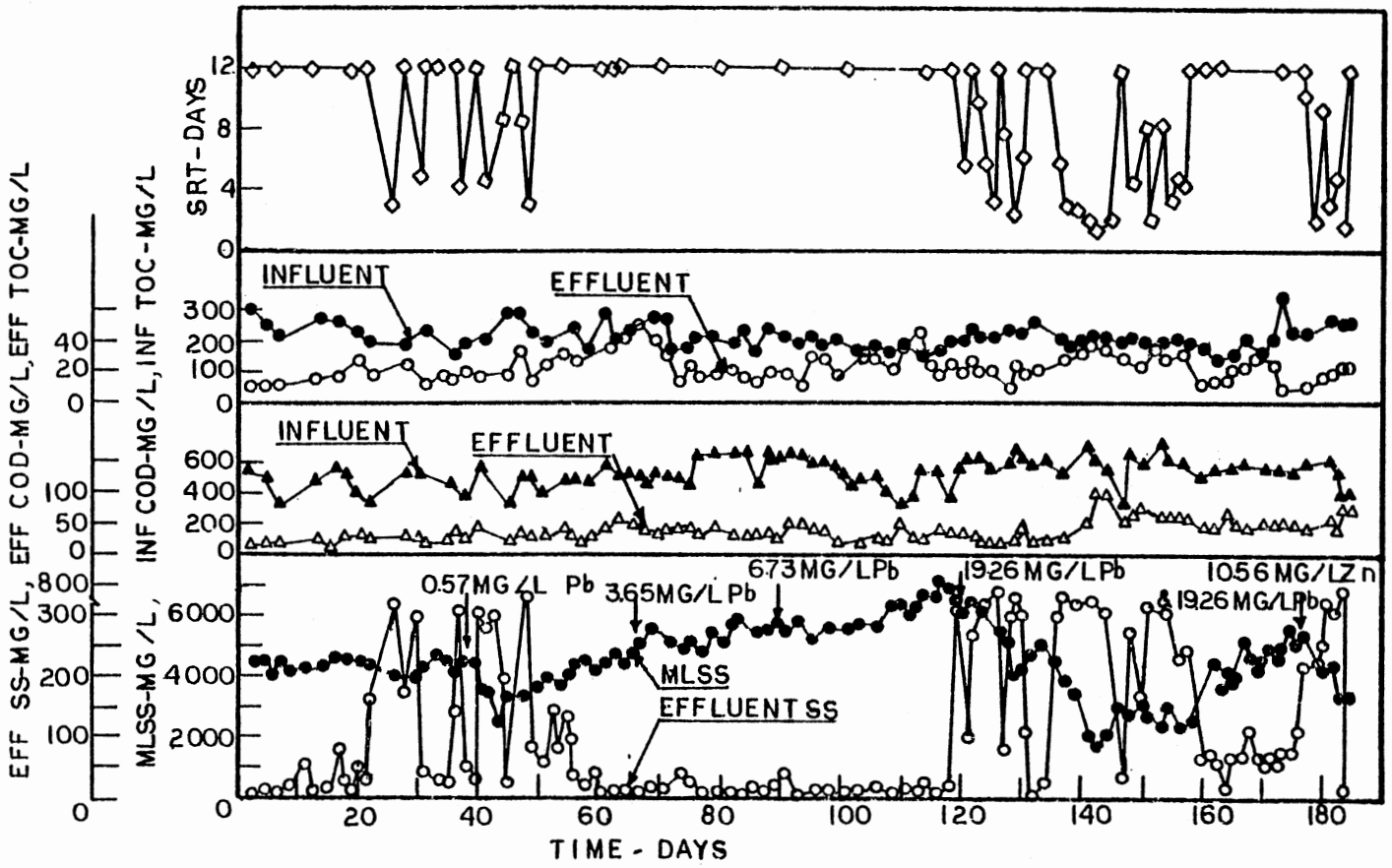

Figure 9. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 12 Days Receiving a Wastewater Composed of Various Dosages of Lead

MLSS concentrations did not vary and effluent suspended solids concentions remained low (less than 20 mg/l). No difficulty was observed in maintaining a constant SRT of three days. Effluent soluble TOC and COD concentrations were not affected by the addition of 0.56 mg/l Pb. On day 42 of the study, the influent lead concentration was increased to 3.32 mg/l. MLSS concentrations decreased from 2000 to 1400 mg/l, but later increased to 2000 mg/l. Effluent suspended solids concentrations exceeded 100 mg/l. Effluent soluble TOC and COD concentrations were basically the same as before even after increasing the dosage of lead to 3.32 mg/l except for a three or four day period (day 49 to 53) during which time effluent TOC and COD exceeded 36 and 60 mg/l, respectively. On day 83 of the study, the influent lead concentration was increased from 3.32 to 5.46 mg/l. MLSS concentrations decreased from 1900 to 1000 mg/l, but later increased to 3000 mg/l. Effluent quality with respect to suspended solids concentration deteriorated, resulting in an effluent suspended solids concentration averaging 39 mg/l. Difficulty in maintaining a constant SRT of 3 day occurred a few days after introduction of 5.46 mg/l lead. Effluent soluble TOC and COD concentrations were affected by increasing influent lead dosage from 3.32 to 5.46 mg/l.

On day 108 of the study, the influent lead concentrations were increased from 5.46 to 18.08 mg/l. MLSS concentrations decreased from 2200 to 13 mg/l and later increased to 2400 mg/l. Effluent suspended solids concentration averaged 76 mg/l. Difficulty in maintaining a constant SRT of three days occurred four days after the addition of 18.08 mg/l lead. Effluent TOC ranged between 20 and 50 mg/l with an average of 33 mg/l.

In general, difficulty in maintaining a constant SRT of three days occurred at influent lead concentrations of 5.46 and 18.08 mg/l. The influent COD and TOC values ranged from 360 to 640 mg/l and 145 to 290 mg/l, respectively. MLSS varied between 1000 mg/l and 3000 mg/l. MLSS concentrations decreased every time the system was subjected to an increased dosage of lead, but later the biomass concentrations increased. The magnitude of the decrease was proportional to influent lead concentration. Effluent suspended solids concentration remained low (less than 20 mg/l) until the influent lead concentration reached 5.46 mg/l. Effluent soluble COD concentrations were basically not affected by influent lead concentration at all dosages except at the dosage of 5.46 mg/l. The average effluent soluble TOC shows the gradual increase with increasing dosage up to 5.46 mg/l of lead. Further increase in the lead concentration to 18.08 mg/l did not result in further increase in effluent soluble TOC.

The operational data of the six day SRT unit which received lead at a concentration of 0.44 mg/l is shown in Figure 8. Because of the high effluent suspended solids which eventually lead to system failure, it was difficult to maintain the SRT at six days. The influent COD and TOC values varied between 440 to 560 mg/l and 190 to 210 mg/l, respectively. It can be seen that addition of lead caused a decrease in MLSS from an initial concentration of 2900 mg/l down to 1000 mg/l within a three-week period. Effluent soluble COD and TOC increased markedly and ranged from 40 to 80 mg/l COD and 36 to 60 mg/l TOC.

Figure 9 represents a system which was operated at a 12 day SRT with various influent lead concentrations. On day 38 of the study the system was subjected to an influent lead concentration of 0.57 mg/l.

Difficulty was encountered in maintaining a constant SRT of 12 days during the period from day 21 to 50. However, on day 38 of the study, lead was added at a dosage of 0.57 mg/l. The MLSS level was depressed after the introduction of an influent lead concentration of 0.57 mg/l. The biomass concentration then started to build up in the reactor and reached 5000 mg/l. Effluent suspended solids concentrations were very high (more than 400 mg/l). Effluent soluble COD and TOC concentrations were affected by influent lead dosage of 0.57 mg/l (3.5% decreasing COD removal efficiency and 4.5% reduction in TOC removal efficiency compared to the control values was observed).

On day 66 of the study, the influent lead concentration was increased from 0.57 to 3.65 mg/l. It can be seen that the unit was maintained at a constant SRT of 12 days. MLSS concentrations decreased from 5400 to 4800 mg/l but later increased to 5600 mg/l. Effluent suspended solids concentrations were low (less than 40 mg/l) during the entire phase of this study. Effluent soluble TOC and COD were not influenced by increasing the influent lead dosage from 0.57 to 3.65 mg/l.

On day 90 of this study, the influent lead dosage was increased from 3.65 to 6.73 mg/l. It can be observed that steady state in terms of SRT was easily achieved. MLSS levels did not change for a period of two weeks but later increased from 5700 mg/l to 7000 mg/l. Effluent suspended solids concentrations remained low, averaging 15 mg/l. Effluent soluble TOC varied between 10 and 46 mg/l and COD between 20 to 55 mg/l.

On day 119 of this study, the influent lead concentration was increased to 19.26 mg/l. Difficulty in maintaining a constant SRT of 12 days was encountered. The MLSS level dropped from 6600 mg/l to 1800 mg/l. Upon addition of an influent lead concentration of 19.26 mg/l,

serious deterioration in effluent suspended solids concentration was noted (average of 212 mg/l). Effluent soluble TOC and COD was within the range of 8 to 40 mg/l and 20 to 100 mg/l, respectively.

On day 176 of this study, a mixture of lead and zinc was added to the system. The result of this phase of the study will be discussed in another section.

In brief, Figure 9 shows that difficulty in operating the reactor at a constant SRT of 12 days was experienced at an influent lead dosage of 19.26 mg/l. However, before the addition of 0.57 mg/l lead, the SRT was fluctuating considerably; so difficulty in maintaining the SRT of 12 days after the addition of 0.57 mg/l lead cannot be attributed to the addition of lead. But this is not the case when the dosage was increased to 19.26 mg/l lead, because before increasing the dosage of lead to 19.26 mg/l, the SRT was maintained at 12 days without any significant fluctuation. So the difficulty encountered in maintaining an SRT of 12 days after increasing the dosage to 19.26 mg/l can be attributed to the increased dosage of lead.

Slight depression of MLSS at a dosage of 3.65 mg/l and no depression of MLS at a dosage of 6.73 mg/l was observed. Effluent suspended solids concentrations were low during the entire run except for the dosage of 0.57 mg/l, which was the initial dosing and 19.26 mg/l which was the highest concentration. Effluent soluble COD and TOC concentrations were both basically unaffected by influent lead dosages compared to the post-dosage condition. However, addition of lead to the unit reduced the removal efficiencies (4 - 6%) in terms of COD and TOC compared with control values.

The effluent characteristics of the unit that received different

lead dosages at various SRTs are shown in Table IX. Removal efficiencies (in terms of COD and TOC) of 90.6, 89.4, 85.4, and 91.6 percent, and 91.8, 85.7, 81.7, and 84.1 percent were attained when lead concentrations of 0.56, 3.32, 5.46, and 18.08 mg/l, respectively, were added to the three day SRT unit. The results in Table IX show the average removal efficiencies in terms of TOC decreased (6 - 10%) as lead dosage increased. However, addition of 0.56 mg/l lead did not have any effect on TOC and COD removal efficiencies and at 18.08 mg/l dosage in terms of COD. Treatment efficiencies in terms of COD and TOC were 89.1 and 74.9 percent, respectively for the six day SRT reactor. The results indicate that treatment efficiency (in terms of TOC) was reduced by 13% compared with control values. The 12 day SRT unit was able to achieve COD removal efficiencies of 92.5, 94.0, 93,7, and 92.1 percent and TOC removal efficiencies of 88.6, 90.3, 86.7, and 88.1 percent when lead concentrations of 0.57, 3.65, 6.73, and 19.26 mg/l, respectively, were introduced. The average treatment efficiency was reduced (2.5 to 4%) in terms of COD and 3-5% in terms of TOC.

Performance of Activated Sludge Systems Receiving Wastewater Containing Zinc

Figures 10 through 12 illustrate the performance of the bench-scale units which received different dosages of zinc at various SRTs (3, 6, and 12 days).

Figure 10 depicts the performance of the reactor which was operated at an SRT of three days. Nine days after the unit reached steady state, it was subjected to an influent zinc dosage of 1.14 mg/l and maintained at a three day SRT. This is shown as day 4 on Figure 10. MLSS

TABLE IX

EFFLUENT CHARACTERSITICS OF THE UNITS RECEIVING LEAD

	SRT = 3 days				SRT = 6 days	SRT = 12 days			
	Influent Lead (Pb) (mg/l)				Influent Lead (Pb) (mg/l)	Influent Lead (Pb) (mg/l)			
	0.56	3.32	5.46	18.08	0.44	0.57	3.65	6.73	19.26
Influent									
Soluble COD (mg/l)	501	405	418	525	504	482	581	523	592
Soluble TOC (mg/l)	219	203	202	208	199	238	222	188	218
Effluent									
Soluble COD (mg/l)	47	43	61	44	55	36	35	33	47
Soluble TOC (mg/l)	19	29	37	33	50	27	21.5	25	26
COD Removal Efficiency (%)	90.6	89.4	85.4	91.6	89.1	92.5	94.0	93.7	92.1
TOC Removal Efficiency (%)	91.8	85.7	81.7	84.1	74.9	88.6	90.3	86.7	88.1
Effluent SS (mg/l)	10	29	39	76	84	134	16	15	212

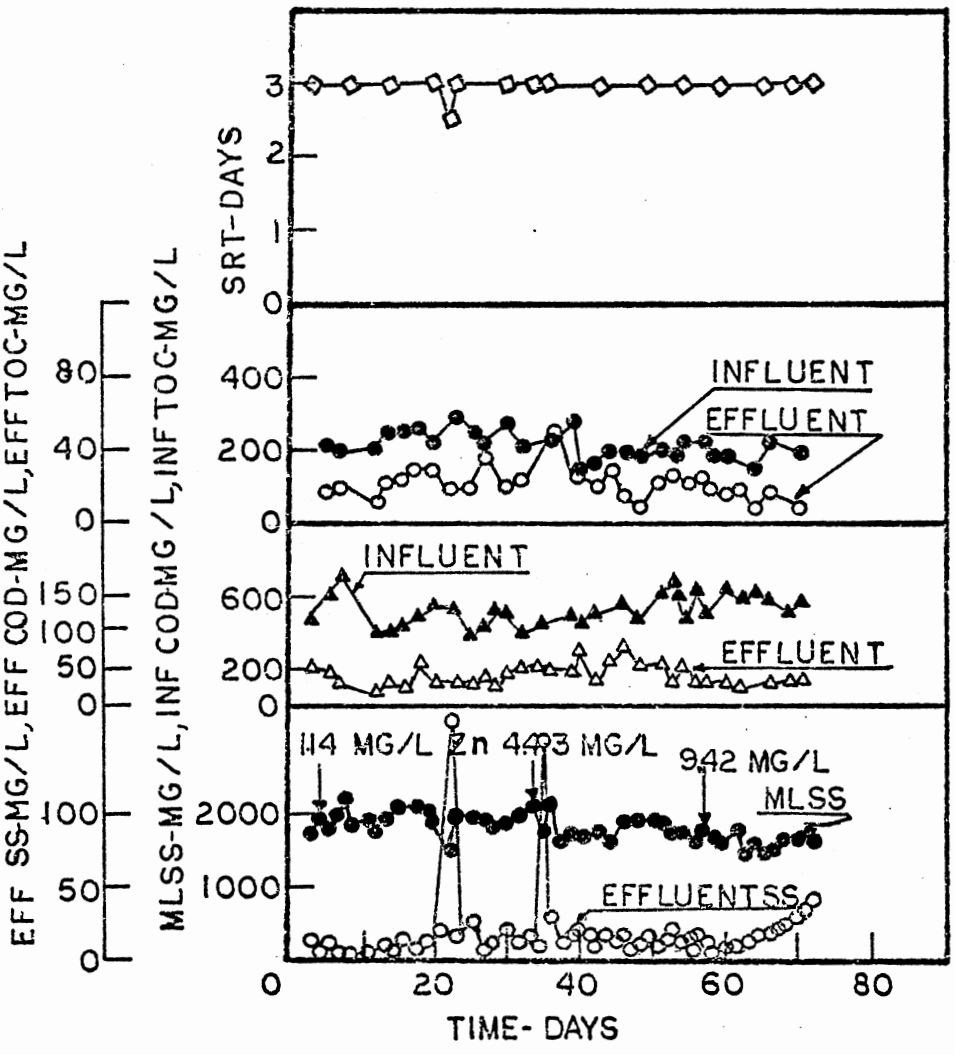

Figure 10. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 3 Days Receiving a Wastewater Composed of Various Dosages of Zinc

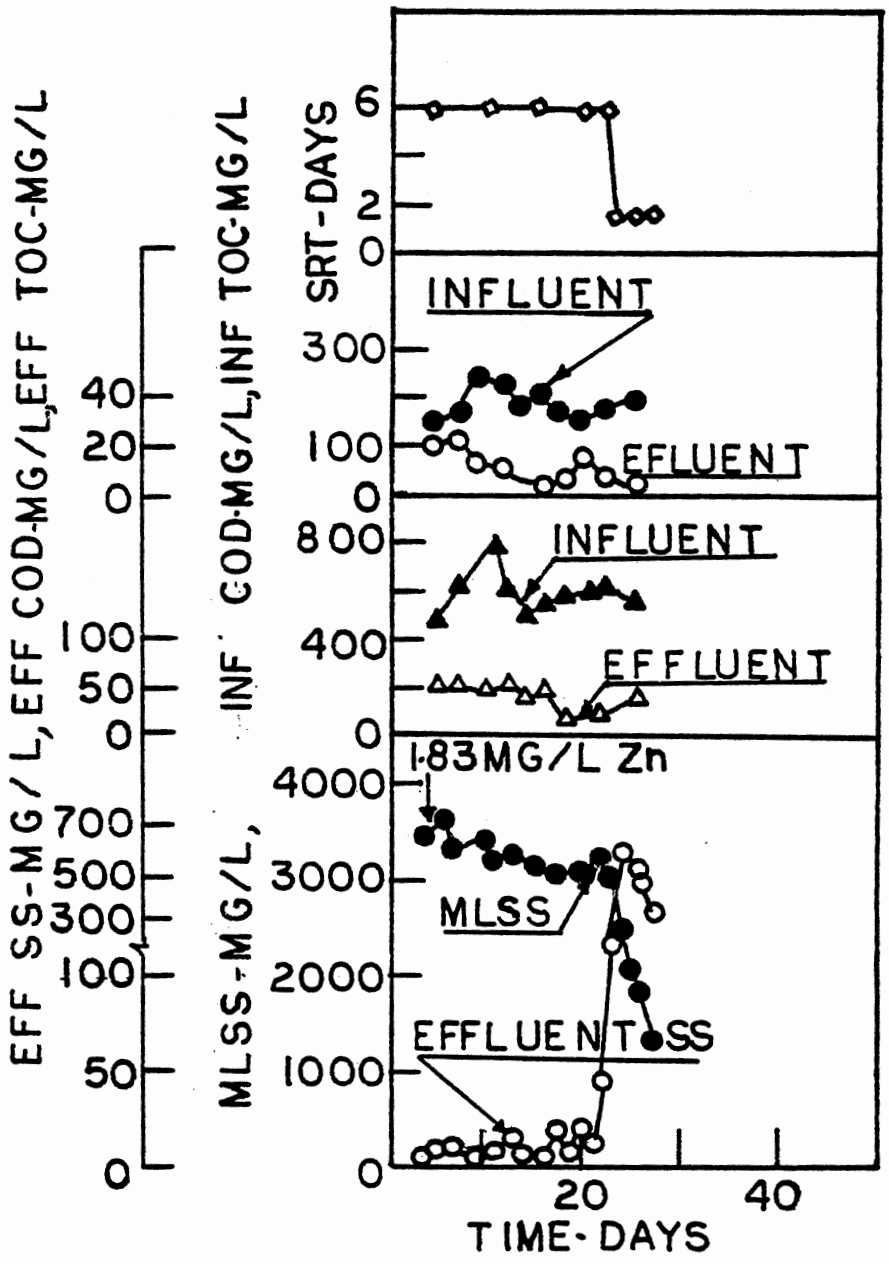

Figure 11. Performance Data for an Activated Sludge Reactor Maintaning at an SRT = 6 Days Receiving a Wastewater Composed of Various Dosages of Zinc

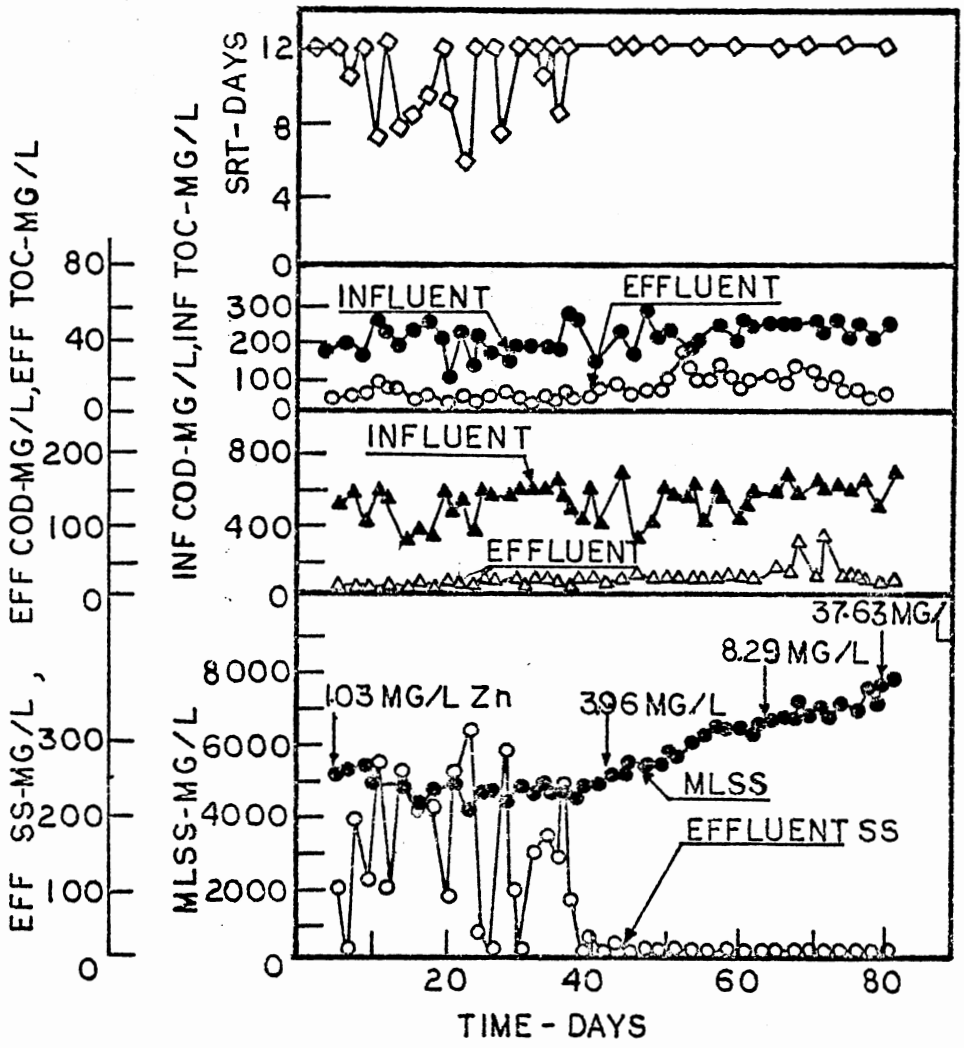

Figure 12. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 12 days Receiving a Wastewater Composed of Various Dosages of Zinc

levels ranged between 1700 and 2200 mg/l. Effluent suspended solids concentrations were within the range of 2 and 27 mg/l. Effluent soluble TOC and COD concentrations fluctuated between 12 and 36 mg/l, and 30 and 60 mg/l, respectively. On day 33 of the study, the influent zinc concentration was increased to 4.43 mg/l. The system was easily maintained at a three day SRT. MLSS concentrations started to decrease upon the addition of 4.43 mg/l influent zinc (from average of 2000 to 1800 mg/l). Effluent suspended solids concentrations were relatively low except on day 35, when it exceeded 100 mg/l. Effluent soluble TOC and COD concentrations varied between 10 and 50 mg/l, and 40 and 67 mg/l, respectively.

On day 57 of the study, the influent zinc concentrations were increased from 4.43 to 9.42 mg/l. Again the system operated at a constant SRT of three days. MLSS concentrations decreased from an average of 1800 mg/l to 1600 mg/l. Addition of zinc at a dosage of 9.42 mg/l caused an increase in effluent suspended solids concentration (approaching 50 mg/l). Effluent soluble TOC and COD varied between 8 and 17 mg/l, and 20 and 30 mg/l, respectively.

Generally, the unit could be accurately maintained at a three day SRT. Influent TOC and COD values fluctuated between 150 and 280 mg/l, and 30 and 700 mg/l, respectively. Introduction of 4.43 mg/l zinc caused MLSS concentration to decrease. This trend continued as 9.42 mg/l was added to the influent. Effluent suspended solids concentrations were relatively constant up to 9.42 mg/l, at which time a steady deterioration was noted. Effluent soluble COD was higher at 4.43 mg/l dosage level than initial dosage level of 1.14 mg/l. Further increase in dosage to 9.42 mg/l actually decreased effluent soluble COD to a level comparable to the initial dosage. Effluent soluble TOC concentrations

were almost the same at the dosage level of 1.14 and 4.43 mg/l. Further increase in zinc dosage to 9.42 mg/l lowered the effluent soluble TOC (from 23 to 14 mg/l). By the time the system was subjected to a dosage of 9.42 mg/l, the biomass had been exposed to zinc for a considerable period of time, enabling the biomass to become acclimated to zinc and to improve its performance even in the presence of the zinc. This resulted in a better quality even at a higher zinc dosage.

Figure 11 presents the effect of an influent zinc concentration of 1.83 mg/l upon a microbial population which had been previously adapted to a zinc-free wastewater at an SRT of six days. The system achieved a fairly good steady state during the first two weeks of operation. At that time, system failure was experienced increased effluent suspended solids and decreased MLSS concentrations. MLSS values gradually decreased during the first two weeks of operation, and then suddenly dropped from 3200 mg/l to 1300 mg/l. It can be seen that effluent suspended solids concentrations were relatively low (less than 20 mg/l) from the two weeks of operation and then increased to 600 mg/l. Effluent soluble COD and TOC varied between 2 mg/l to 22 mg/l and 10 mg/l to 50 mg/l, respectively. Even though the unit lost most of its biomass, it could still remove influent substrate with biomass left in the reactor (93.6% removal efficiency in terms of COD and 94.3% in terms of TOC).

Operational data of the unit which was run at a 12 day SRT is shown in Figure 12. After 76 days of operation, the system was subjected to 1.03 mg/l zinc. This is shown as day 5 on Figure 12. Some difficulties were encountered in maintaining the SRT at 12 days. This was probably due to the fact that the biomass was exposed to the zinc for the first time. The level of MLSS was relatively constant (average 4800 mg/l)

during the time when the microorganisms were exposed to a zinc dosage of 1.03 mg/l. Effluent suspended solids concentrations were quite high (often greater than 100 mg/l) during the period when the influent zinc concentration was 1.03 mg/l. Effluent soluble COD and TOC values ranged between 15 and 35 mg/l, and 6 and 15 mg/l, respectively. On day 42 of the operation, the zinc in the feed solution was increased to 3.96 mg/l. The system operated at a fairly steady state condition at 12 day SRT. MLSS concentrations in the reactor began to increase (from 5200 to 6500 mg/l), and effluent suspended solids concentrations were low (less than 30 mg/l). Effluent soluble solids concentrations were low (less than 30 mg/l). Effluent soluble COD and TOC concentrations were within the range of 25 and 40 mg/l, and 10 and 34 mg/l, respectively.

On day 64 of the study, 8.29 mg/l zinc was added to the unit, and a steady SRT of 12 days was achieved. MLSS concentrations in the unit continued increasing from 6800 to 7200 mg/l, and effluent suspended solids concentrations were still low (ranging between 0 and 15 mg/l). Effluent soluble COD and TOC values fluctuated between 25 and 90 mg/l and 9 and 26 mg/l, respectively.

In brief, some difficulties were observed in maintaining an SRT of 12 days when the unit was exposed to 1.03 mg/l zinc. However, at higher influent zinc dosages, a 12 day SRT could be accurately controlled. By the time the system was subjected to a dosage of 8.29 mg/l, the system had been exposed to zinc for a period of 63 days. Influent substrate in terms of TOC was within the range of 100 and 280 mg/l. Influent COD varied between 320 and 700 mg/l, with an average of 590 mg/l. As can be observed in Figure 12, the MLSS concentration in the unit increased as the influent zinc dosage increased except at a zinc dosage of 1.03 mg/l. Influent zinc

dosages of 3.96, 8.29, 20.17, and 37.63 mg/l produced low effluent suspended solids, yet effluent suspended solids concentrations were fairly high at a zinc loading of 1.03 mg/l. Effluent soluble COD was affected by increases in influent zinc concentrations from 1.03 to 3.96 and from 3.96 to 8.29 mg/l.

The effluent characteristics of the units receiving zinc were presented in Table X. At zinc dosages of 1.14 mg/l, 92.5% of the COD and 89.2% of the TOC were removed by the three day SRT reactor. At a loading of 4.43 mg/l zinc, the same reactor was capable of removing 89.9% of the COD and 88.8% of the TOC. At the highest loadings of 9.42 mg/l zinc, the three day unit removed 94.8% of the COD and 92.4% of the TOC. The average treatment efficiency in terms of COD was reduced by 2% when zinc was increased from the initial dosage level of 1.14 to 4.43 mg/l. Further increase in dosage to 9.42 mg/l improved treatment efficiencies in terms of COD and TOC compared with the initial dosage and control values. Treatment efficiencies in terms of COD and TOC were 93.6 and 94.3 percent, respectively, for the six day SRT unit. The results in Table X indicate that addition of a zinc dosage of 1.83 mg/l had no effect on removal efficiencies in terms of COD and TOC. The 2 day SRT unit was able to produce COD removal efficiencies of 95.1, 94.2, 94.5, 96.5, and 96.5 percent when zinc concentrations of 1.03, 3.96, 8.29, 20.17, and 37.63 mg/l, respectively, were added. At these same zinc dosages the TOC removal efficiencies were 94.7, 91.6, 92.9, 97.0, and 96.0 percent. The results indicate that the removal efficiency for a zinc dosage of 3.96 mg/l was about one percent lower in terms of COD and three percent lower in terms of TOC than for the initial dosage of 1.03 mg/l.

TABLE X

EFFLUENT CHARACTERISTICS OF THE UNITS RECEIVING ZINC

	SRT = 3 days			SRT = 6 days	SRT = 12 days				
	Influent Zinc (Zn) (mg/l)			Influent Zinc (Zn) (mg/l)	Influent Zinc (Zn) (mg/l)				
	1.14	4.43	9.42	1.83	1.03	3.96	8.29	20.17	37.63
Influent									
Soluble COD (mg/l)	491	537	578	577	528	534	617	635	625
Soluble TOC (mg/l)	223	205	158	195	190	215	239	231	224
Effluent									
Soluble COD (mg/l)	37	54	30	37	26	31	34	22	22
Soluble TOC (mg/l)	24	23	14	11	10	18	17	7	9
COD Removal Efficiency (%)	92.5	89.9	94.8	93.6	95.1	94.2	94.5	96.5	96.5
TOC Removal Efficiency (%)	89.2	88.8	92.4	94.3	94.7	91.6	92.9	97.0	96.0
Effluent SS (mg/l)	22	27	33	109	128	13	7	12	8

Performance of Activated Sludge Systems Receiving Wastewater Containing Cadmium

The response of those units that received various concentrations of cadmium and operated at 3, 6, and 20 day SRT is depicted in Figures 13 through 15. Figure 13 shows the performance of the reactor which was operated at an SRT of 3 days. After 19 days of operation, 4.06 mg/l cadmium was introduced to the system. This is shown as day 8 on Figure 13. As can be seen in Figure 13, a three day SRT was maintained during the addition of 4.06 mg/l cadmium. MLSS concentrations started to decrease from 1800 to 1400 mg/l, but then increased from 1400 to 1900 mg/l. During the first two weeks of operation at 4.06 mg/l cadmium, the effluent solids concentration was low but subsequently, the solids concentration increased substantially and fluctuated considerably. This could have been due to a change in predominance and secondary response of the biomass. Effluent suspended solids concentrations were quite high, averaging 54 mg/l, and especially high during the latter part of the cadmium dosage of 4.06 mg/l. Effluent soluble TOC concentrations were particularly high throughout the 4.06 mg/l influent concentration (averaging 29 mg/l and ranging up to 50 mg/l).

On day 31, cadmium was increased from 4.06 mg/l to 6.02 mg/ cadmium. Again, the 3 day SRT was controlled during administration of 6.02 mg/l cadmium. MLSS levels increased from 1900 mg/l to 2400 mg/l at this cadmium dosage. Effluent suspended solids concentrations were very erratic until day 42, when they fell below 50 mg/l. The effluent TOC was high at the beginning of this loading, but decreased to 10 mg/l on day 49.

On day 50 of the study, the influent cadmium concentration was

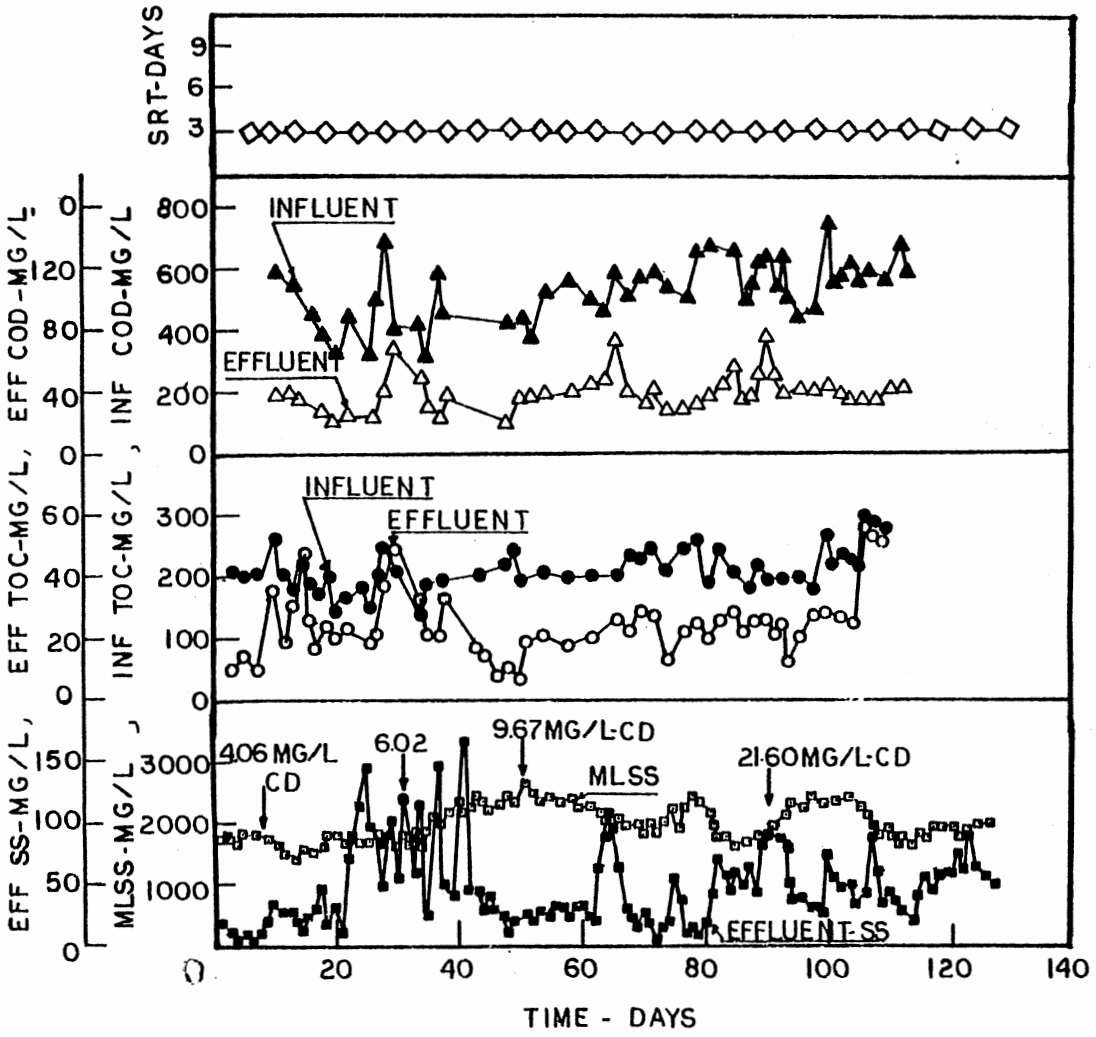

Figure 13. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 3 days Receiving a Wastewater Composed of Various Dosages of Cadmium

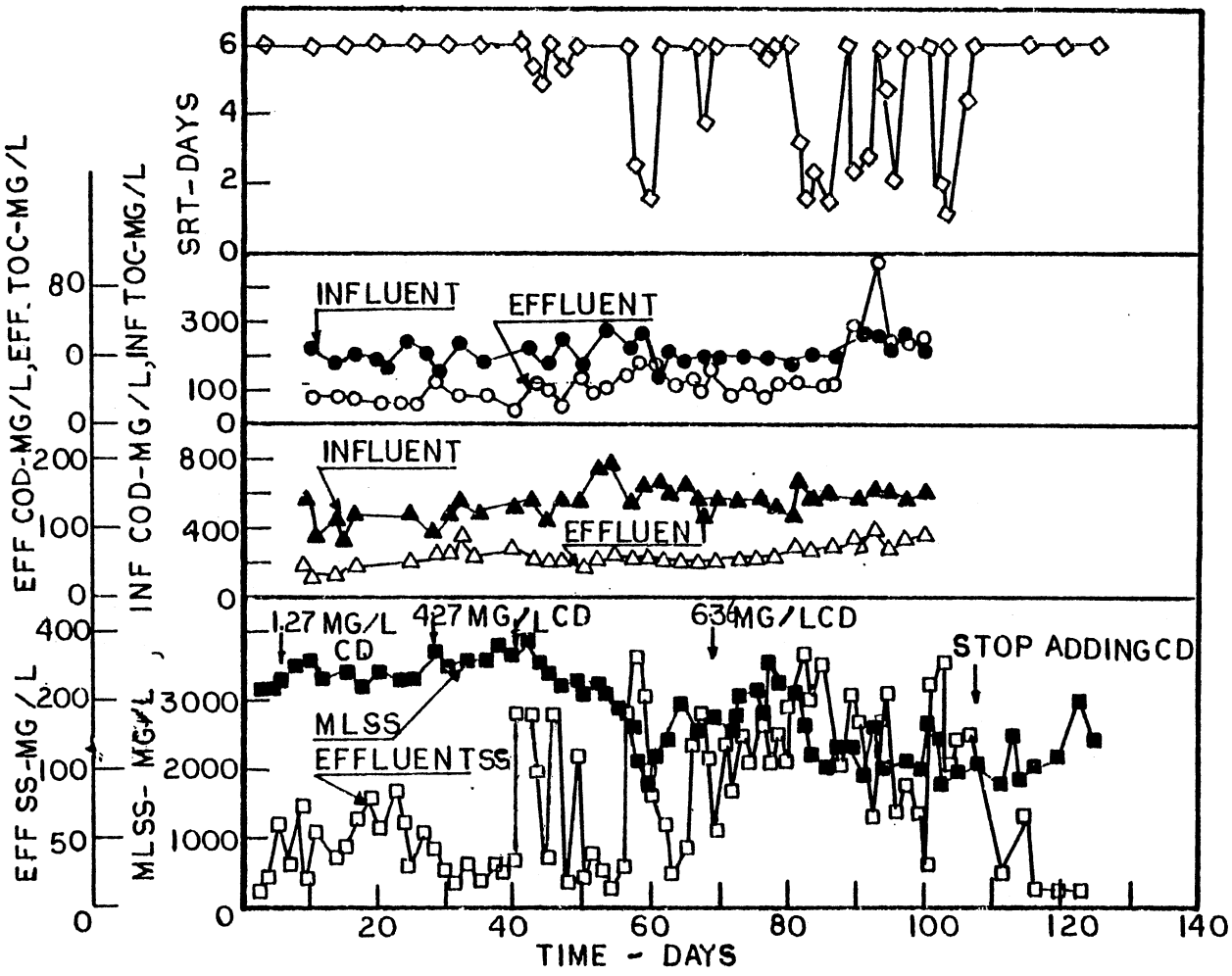

Figure 14. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 20 days Receiving a Wastewater Composed of Various Dosages of Cadmium

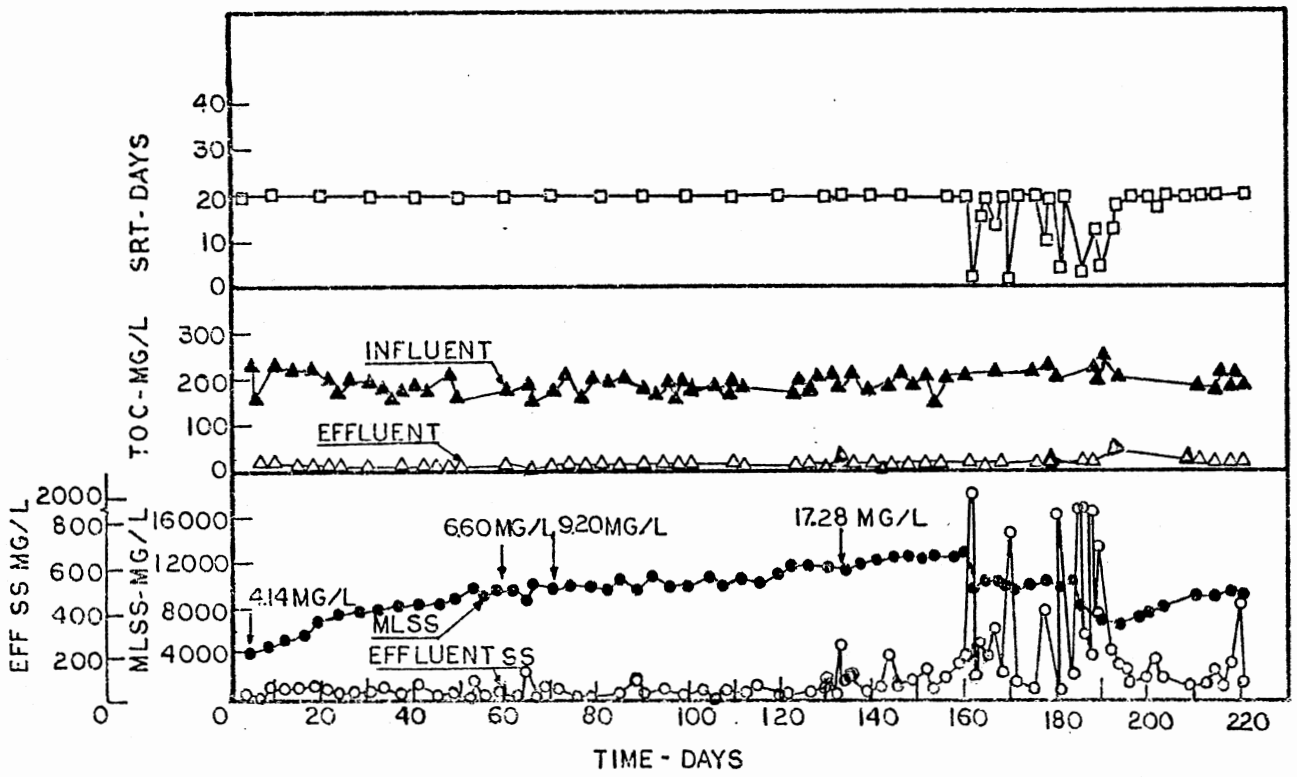

Figure 15. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 20 days Receiving a Wastewater Composed of Various Dosages of Cadmium

increased from 6.02 to 9.67 mg/l. It can be observed that the system operated at steady state during this period. MLSS concentrations remained fairly constant but were reduced from 2400 mg/l to 1800 mg/l. Effluent suspended solids concentrations averaged approximately 25 mg/l for the first 10 days, and then rose to 100 mg/l. They then again decreased to 20-25 mg/l but were very erratic during the remainder of this dosage. The effluent TOC remained fairly low during this period, varying between 12 and 30 mg/l.

On day 90, 21.60 mg/l cadmium was added to the unit. A three day SRT was accurately maintained during the addition of the 21.60 mg/l cadmium. The MLSS concentration began to increase upon addition of 21.60 mg/l cadmium. This increase was then followed by a reduction in MLSS concentrations in the reactor. Effluent suspended solids concentrations ranged between 20 and 100 mg/l, with a great amount of fluctuation. Effluent soluble COD was within the range of 62 and 90 mg/l.

The influence of various influent cadmium dosages (1.27, 4.27, and 6.36 mg/l) on the operation of the activated sludge system maintained at an SRT of 6 days is shown in Figure 14. After 63 days of operation, the reactor received wastewater containing 1.27 mg/l cadmium. This is shown as day 7 on Figure 14. No difficulty was experienced in maintaining an SRT of 6 days. MLSS concentrations averaged 3400 mg/l, which was slightly higher than before the unit received the cadmium concentration of 1.27 mg/l. Effluent suspended solids concentrations fluctuated between 15 and 8 mg/l, averaging 52 mg/l. Effluent soluble COD and TOC values varied between 30 and 50 mg/l, and 10 and 20 mg/l, respectively.

On day 24 of the study, the influent cadmium concentration was increased from 1.27 to 4.27 mg/l. As seen in Figure 14, the steady state

in terms of SRT was not maintained. When the influent cadmium concentration was increased to 4.27 mg/l, MLSS concentrations increased to 3800 mg/l and then decreased to 1700 mg/l, at which time the control over the SRT was lost. The 4.27 mg/l cadmium generated a very high effluent suspended solids concentration (averaging 102 mg/l). Effluent quality, with respect to effluent soluble TOC and COD values, ranged between 6 and 36 mg/l and 40 and 90 mg/l, averaging 22 and 60 mg/l, respectively. The cadmium concentration of 4.27 mg/l seemed to have very little effect on the effluent TOC and COD.

On day 70, the cadmium concentration in the feed solution was increased from 4.27 to 6.36 mg/l. Many difficulties were experienced in maintaining an SRT of 6 days when the influent cadmium concentration was 6.36 mg/l. MLSS concentrations in the reactor increased from 2700 mg/l to 3600 mg/l, and later decreased to 1800 mg/l, at which time the SRT of 6 days could not be controlled. Effluent suspended solids concentrations generally greater than 140 mg/l were observed with a great deal of variability. Effluent soluble COD and TOC values increased to 100 mg/l and 60 mg/l, respectively (averaging 71 and 36 mg/l). On day 108, cadmium was no longer fed to the unit, and it is seen that the system began to recover.

In brief, Figure 14 shows that difficulties were experienced in maintaining an SRT of 6 days, particularly in influent cadmium concentrations in excess of 6.36 mg/l. Influent TOC concentrations varied between 145 and 280 mg/l, with an average of 210 mg/l. Influent substrate in terms of COD was within the range of 340 and 760 mg/l, with an average of 550 mg/l. MLSS concentrations were affected by influent cadmium concentrations. This influence became significant as influent cadmium dosages increased. During the 4.27 and 6.36 mg/l dosages, deterioration of effluent quality with

respect to the effluent suspended solids concentration was rather high. Effluent soluble COD and TOC values were only slightly affected by increases in influent cadmium concentrations. Increasing the influent cadmium concentration did result in a slight further increase in effluent soluble COD and TOC concentrations. It can be noted that profuse foam was observed in the aeration basin and increased with increasing influent cadmium concentration. On day 105, cadmium addition to feed solution was discontinued. It was observed that the foaming ceased, the effluent suspended solids concentration decreased, and control over the SRT was regained.

Figure 15 shows the response of the activated sludge system operating at SRT of 20 days at various influent cadmium concentrations (4.14, 6.60, 9.20, and 17.28 mg/l). After 53 days of operation, the system received wastewater containing a cadmium dosage of 4.14 mg/l. This is shown as day 4 in Figure 15. The unit was operated at a constant SRT of 20 days while influent cadmium concentration was 4.14 mg/l. MLSS concentrations gradually increased to 9600 mg/l. Effluent suspended solids concentrations were rather low (less than 100 mg/l) with an average of 45 mg/l and the effluent soluble TOC was also low (less than 15 mg/l), averaging 12 mg/l.

On day 59, the influent cadmium concentration was increased from 4.14 to 6.60 mg/l. The reactor was accurately maintained at an SRT of 20 days. MLSS concentrations did not change, averaging 9800 mg/l. Effluent suspended solids concentrations varied between 0 and 120 mg/l, with an average of 34 mg/l. The effluent soluble TOC concentration was low, averaging 5 mg/l.

On day 70 of the study, the influent cadmium concentration was increased to 9.20 mg/l. Again control over an SRT of 20 days was accurate. MLSS concentrations increased from 9800 to 12,000 mg/l. Effluent

suspended solids concentrations ranged between 0 and 100 mg/l, with an average of 47 mg/l. Effluent soluble TOC concentrations were low and less than 20 mg/l. The system was still efficient (92.9% removal efficiency) in removing influent substrate in terms of TOC.

On day 133 of this study, the 17.28 mg/l cadmium was added to the unit. It was very difficult to control an SRT of 20 days. MLSS concentrations increased from 12,000 to 13,000 mg/l, then suddenly decreased due to solids washout in the effluent. On day 196 of the study, MLSS began to increase, and control over SRT was regained. Four weeks after adding 17.28 mg/l, very high effluent suspended solids concentrations were observed (as high as 2200 mg/l). Again, as control over SRT was regained, effluent suspended solids concentrations decreased to the previous low level. With exception of the period where control over SRT was lost, effluent soluble TOC values were relatively constant, averaging 17 mg/l.

Generally, as can be seen in Figure 15, accurate control over the SRT was maintained while influent cadmium concentrations were increased from 4.14 to 9.20 mg/l. Four weeks after the addition of 17.28 mg/l it became impossible to control an SRT of 20 days due to the high effluent suspended solids concentration. Influent substrate with respect to TOC varied between 140 mg/l and 250 mg/l. MLSS concentrations gradually increased to 13,000 mg/l and then deteriorated upon addition of the 17.28 mg/l dosage. Effluent suspended solids concentrations were rather low (less than 100 mg/l) during the 4.14, 6.60, and 9.20 mg/l dosages.

Table XI shows the effluent quality in terms of COD, TOC, and suspended solids for the cadmium-fed units. COD removal efficiencies of 85.2, 84.4, 85.3, and 86.6 percent, and TOC removal efficiencies of

TABLE XI

EFFLUENT CHARACTERISTICS OF THE UNITS
RECEIVING CADMIUM

	SRT = 3 days				SRT = 6 days			SRT = 20 days			
	Influent Cadmium (Cd) (mg/l)				Influent Cadmium (Cd) (mg/l)			Influent Cadmium (Cd) (mg/l)			
	4.06	6.02	9.67	21.60	1.27	4.27	6.36	4.14	6.60	9.20	17.28
Influent											
Soluble COD (mg/l)	479	435	573	603	437	579	579	488	510	482	562
Soluble TOC (mg/l)	202	202	215	240	202	208	213	201	171	185	206
Effluent											
Soluble COD (mg/l)	71	68	84	81	44	60	71	16	18	20	55
Soluble TOC (mg/l)	29	20	24	32	15	22	36	12	5	13	17
COD Removal Efficiency (%)	85.2	84.4	85.3	86.6	89.9	89.6	87.7	96.7	96.5	95.9	90.2
TOC Removal Efficiency (%)	85.6	90.1	88.8	86.7	92.6	89.4	83.1	94.0	97.1	92.9	91.7
Effluent SS (mg/l)	54	72	40	49	52	102	238	45	34	47	227

85.6, 90.1, 88.8, and 82.9 percent, respectively, were achieved when cadmium concentrations of 4.06, 6.02, 9.67, and 21.60 mg/l were fed to the 3 day SRT unit. The results indicate that addition of cadmium at all four dosages reduced treatment efficiencies (about 6%) in terms of COD when compared with control values. It was found that for the 6 day SRT unit, COD removal efficiencies of 89.9, 89.6, and 87.7 percent were obtained upon introduction of wastewaters containing 1.27, 4.27, and 6.36 mg/l cadium, respectively. Addition of cadmuium at 6.36 mg/l reduced the removal efficiencies 2.3% and 5.9% in terms of COD and TOC, respectively, when compared with control values. Treatment efficiencies of 96.7, 96.5, 95.9, and 90.2 percent (with respect to COD) were achieved when the 20 day SRT unit received influent cadmium concentrations of 4.14, 6.60, 9.20, and 17.28 mg/l, respectively. Addition of cadmium to the 20 day SRT unit did not have any impact on removal efficiency except for cadmium influent concentration of 17.28 mg/l. At this concentration, treatment efficiencies in terms of COD and TOC were reduced by 6% and 2.7%, respectively, compared with control values.

Sludge Settleability

Sludge volume index (SVI) and zone settling velocity (ZSV) were utilized to evaluate the settling properties of the control and test reactors. A MLSS concentration of 900, 1900, 2100, and 4800 mg/l were selected for the control units and test reactors as a basis for the comparison. A capillary suction time (CST) apparatus was employed to assess the dewaterability of the sludge.

Tables XII, XIII, and XIV summarize the settleability and dewaterability of the activated sludge systems which received either

TABLE XII

SETTLING AND DEWATERING CHARACTERISTICS OF THE CONTROL UNITS AND THE UNITS RECEIVING LEAD

SRT = 3 days

Lead Influent (mg/l)	MLSS = 900 mg/l						MLSS = 1800 mg/l		
	SVI (ml/g)	ZSV (ft/d)	CST (second)	SVI	ZSV	CST	SVI (ml/g)	ZSV (ft/d)	CST (second)
Control	483	51.09	7.7				426	23.14	8.2
0.56	643	20.8	5.2				462	3.15	5.3
3.32	1035	4.23	5.0				573	0.86	5.5
5.46	185	214.27	5.5						
18.08	876	15.31	6.6				481	0.57	7.4

SRT = 12 days

	MLSS = 900 mg/l			MLSS = 2100 mg/l			MLSS = 4800 mg/l		
Control	409	75.95	7.3	406	11.31	5.9	208	2.21	7.1
0.57	638	46.22	6.5	416	3.86	8.3	223	0.69	7.8
3.65	141	321.84	6.4	180	54.43	8.3	---	---	---
6.73	255	169.34	8.5	420	9.18	8.8	---	---	---
19.26	---	----	---	314	18.14	243.5	207	2.69	53

TABLE XIII

SETTLING AND DEWATERING CHARACTERISTICS OF THE CONTROL UNITS AND THE UNITS RECEIVING ZINC

SRT = 3 days

Zinc Influent (mg/l)	MLSS = 900 mg/l			MLSS = 1900 mg/l		
	SVI (ml/g)	ZSV (ft/d)	CST (second)	SVI (fm/q)	ZSV (ft/d)	CST (second)
Control	483	51.09	7.7	426	23.14	8.2
1.14	641	56.45	7.1	427	12.48	7.7
4.43	673	28.95	9.6	561	4.09	10.10
9.42	---	---	---	317	36.4	10.0

SRT = 6 days

	MLSS = 3100 mg/l			MLSS - 1900 mg/l		
Control	125	74.52	9.0	94	298.00	8.9
1.83	406	1.06	7.0	542	0.00	---

SRT = 12 days

	MLSS = 900 mg/l			MLSS = 2100 mg/l			MLSS = 4800 mg/l		
Control	409	75.95	7.3	406	11.31	5.9	208	2.21	7.1
1.03	265	144	8.2	428	4.03	7.7	205	0.84	8.5
3.96	172	259.20	8.2	334	15.03	7.4	---	---	---
8.29	177	522.72	10.3	182	61.71	9.7	---	---	---

TABLE XIV

SETTLING AND DEWATERING CHARACTERISTICS OF THE CONTROL UNITS AND THE UNITS RECEIVING CADMIUM

Cadmium Influent (mg/l)	MLSS = 900 mg/l SVI (ml/g)	ZSV (ft/d)	CST (second)	SVI	ZSV	CST	MLS = 1900 mg/l SVI (ml/g)	ZSV (ft/d)	CST (second)
				SRT = 3 days					
Control	483	51.09	7.7				426	23.14	8.2
4.06	387	23.76	14.0				554	0.66	15.8
6.02	640	115.19	14.4				397	2.56	15.0
9.67	2135	144.00	24.6				381	20.62	19.6
21.60	720	27.65	9.5				512	1.26	11.3
				SRT = 6 days					
Control	125	74.52	-	94	298.00	8.9	241	13.87	7.2
1.27	140	518.40	7.6	-	-	-	298	0.71	10.9
4.27	737	1.46	8.6	-	-	-	-	-	-
6.36	934	6.31	7.7	507	5.46	9.5	-	-	-
				SRT = 20 days					
Control	148	1.25	6.8				-	-	-
4.17	159	1.13	6.5				-	-	-
9.20	130	2.17	10.1				138	43.20	10.1
17.28	159	0.77	15.3				282	0.47	-

lead, zinc, or cadmium at various concentrations and at different solids retention times, respectively. These results are an average of several tests performed during each operational condition.

Settleability and Dewaterability for Lead-fed Units

As can be seen from Table XII, sludge settleability as measured by zone settling velocity and sludge volume index, indicated that increasing lead concentrations caused poor settling in the 3 day SRT unit except at the dosage of 5.46 mg/l. Settleability of the 12 day SRT unit was generally unaffected by influent lead concentrations.

Dewaterability as measured by capillary suction time appeared to be improved slightly by influent lead concentrations at the 3 day SRT unit. The addition of lead caused a reduction in dewaterability of the sludge for the 12 day SRT unit. Unusual operational conditions whereby large quantities of higher forms of biological life were present in the aeration basin may have accounted for high CST (53 and 243.5 second) readings recorded in the 12 day SRT unit when the influent lead concentration was 19.26 mg/l.

Settleability and Dewaterability for Zinc-fed Units

As can be observed from Table XIII, sludge settleability for the 3 day and 6 day SRT units were reduced (from 23.14 to 4.09 ft/d) by increasing zinc concentrations, while at the 12 day SRT condition, increasing zinc concentration (from 1.14 to 9.42 mg/l) improved settleability (increased from 76 to 522.72 ft/d). Sludge dewaterability was reduced by 9% for the 3 day SRT and 16.4 to 39.2 percent for 12 day SRT unit in comparison with control values by incrasing the influent zinc concentration.

Settelability and Dewaterability for Cadmium-fed Units

Table XIV shows the sludge settling and dewatering characteristics of systems which received cadmium at different concentrations. For the most part, results indicated that increasing influent cadmium concentrations diminished the sludge settleability compared with control values. CST data showed that increasing influent cadmium concentrations significantly reduced (19.0 to 68.7%) the dewaterability of sludge of the 3 day SRT. CST of the 6 day SRT unit was reduced by 6.3% to 33.9%, and the dewaterability of sludge of the 20 day SRT unit was reduced by 32.7% to 55.5 percent.

Oxygen Uptake Rate

The oxygen uptake rate data of the control system along with data collected from the systems which received either cadmium, lead, or zinc at various concentrations have been depicted by Table XV. It can be seen that the oxygen uptake rate was reduced upon addition of influent cadmium dosages of 6.02, 9.67, and 21.60 mg/l for the 3 day SRT unit. The oxygen uptake rate of the 6 day SRT system was diminished (12.8%) when cadmium was added at a concentration of 1.27 mg/l. No impact was observed on oxygen uptake rate of the 6 day SRT unit at 4.06 and 6.02 mg/l cadmium. The oxygen uptake rate of 20 day SRT system was reduced (38.4 and 26.1%) at high concentrations (9.20 and 17.28 mg/l) of cadmium.

Upon additions of lead dosages of 0.56 and 5.46 mg/l to the 3 day SRT unit, the oxygen uptake rate was reduced by 22.1% and 10.7 percent, respectively, of the control values. The oxygen uptake rate of

12 day SRT system was reduced by 25.2% and 11.6 percent when the system was subjected to 5.46 and 18.08 mg/l lead, respectively.

The results in Table XV indicate that when compared to the control system, a reduction of 10.7 percent in the oxygen uptake rate was observed when zinc at a loading of 1.14 mg/l was added to the 3 day SRT system. It can also be seen that the oxygen uptake rate of 3 day SRT system was reduced by 17.7 percent upon addition of zinc at a dosage of 4.43 mg/l compared to the control value. Upon addition of zinc at a dosage of 9.42 mg/l to the 3 day SRT unit, the oxygen uptake was reduced by 4.4 percent of the control value. The data in Table XV indicate that zinc at a concentration of 1.14 mg/l had no effect on the oxygen uptake rate of the 6 day SRT system. Oxygen uptake rates decreased as zinc concentrations increased for the 12 day SRT unit.

Development of Biokinetic Constants

The importance of the biokinetic constants in design of wastewater facilities has been realized for years. The scope of this part of the study is to develop the biological constants of synthetic wastewaters and wastewaters containing heavy metal at various concentrations.

The data which were collected during the study were then employed to determine the biokinetic constants for the Kincannon and Stover, modified Eckenfelder, and Lawrence and McCarty models. An example of one set of plots utilized to compute these biokinetic constants required for design of the activated sludge process which received synthetic wastewaters containing no metal can be found in Figures 16 through 25. Graphical determination of all constants are shown with respect to both COD and TOC. Figures 16 and 17 show the plot of the reciprocal of substrate

TABLE XV

OXYGEN UPTAKE RATE OF THE CONTROL UNITS AND THE UNITS RECEIVING CADMIUM, LEAD AND ZINC

		Oxygen Uptake Rate mg/g/hr											
		Influent Cd mg/l					Influent Pb mg/l				Influent Zn mg/l		
SRT	Control	1.27	4.06	6.02	9.67	21.60	0.56	3.32	5.46	18.08	1.14	4.43	9.42
3	15.8	---	20.1	9.7	11.5	14.6	12.3	16.2	14.1	17.4	14.1	13.0	15.1
6	10.9	9.5	12.9	14.3	---	---	---	---	---	---	11.6	---	---
12	9.5	---	---	---	---	---	14.0	9.4	7.1	8.4	9.3	9.1	7.4
20	6.5	---	---	---	4.0	4.8	---	---	---	---	---	---	---

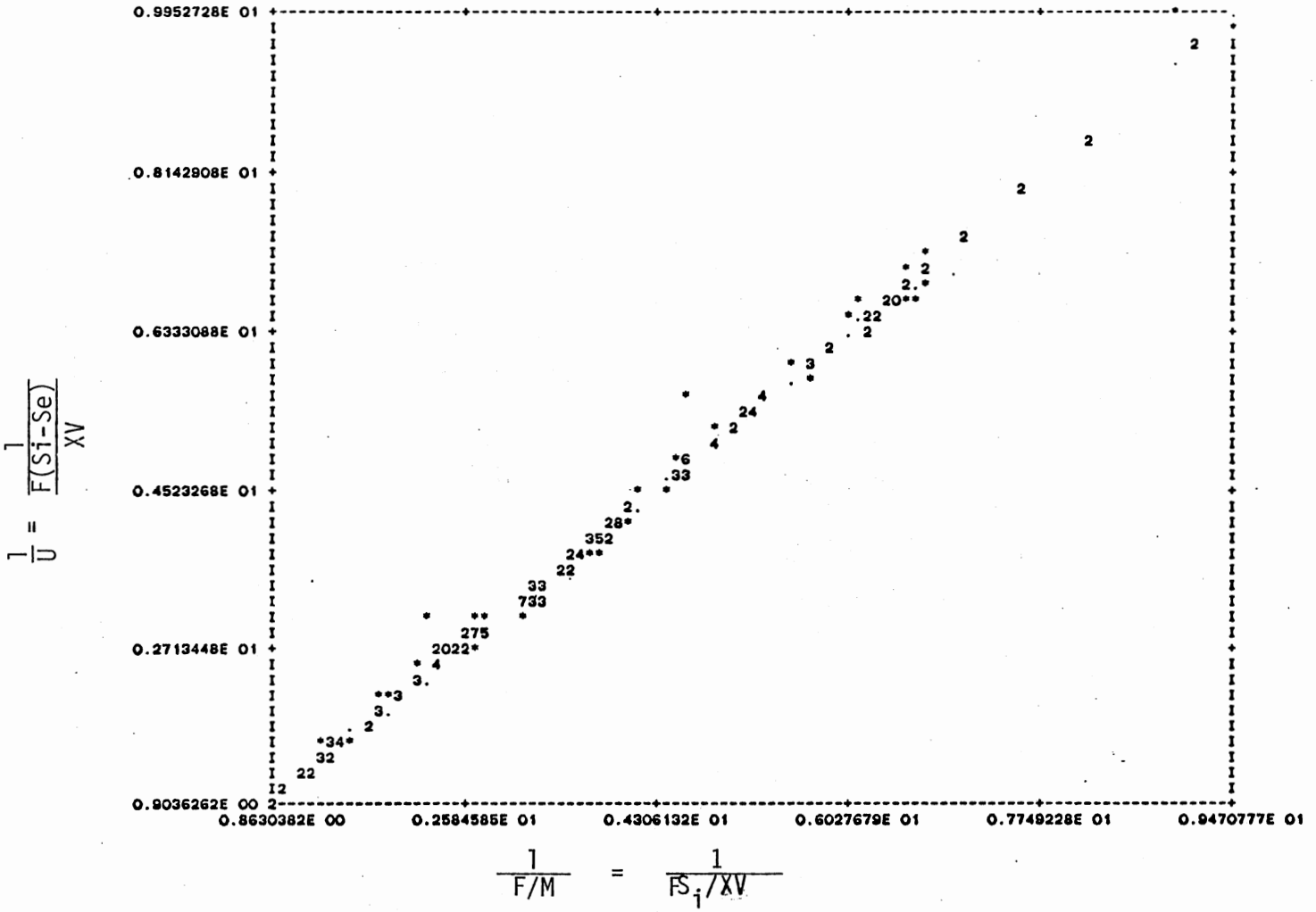

Figure 16. Graphical Determination of k_B and U_{max} in Terms of COD

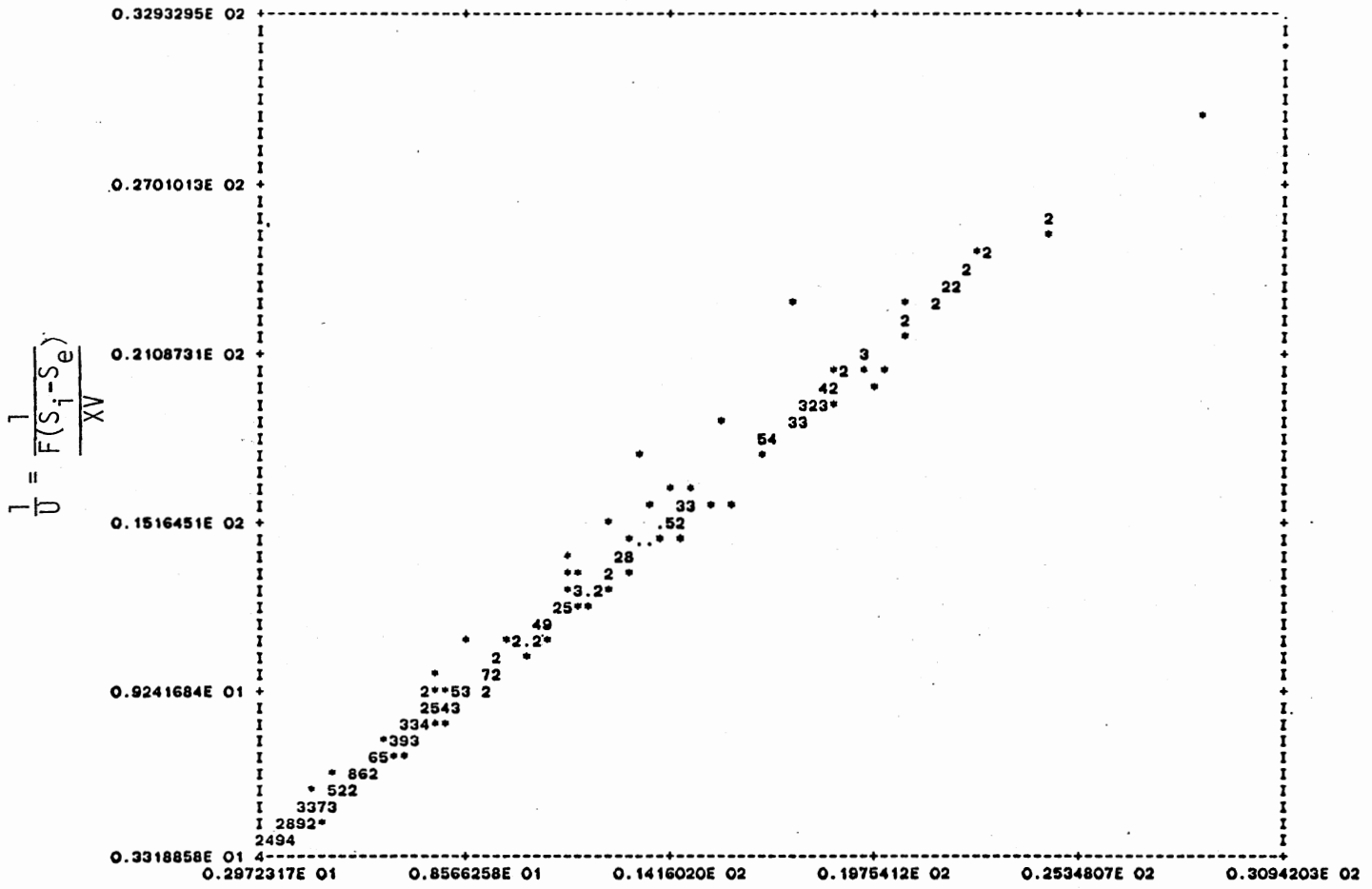

Figure 17. Graphical Determination of k_B and U_{max} in Terms of TOC

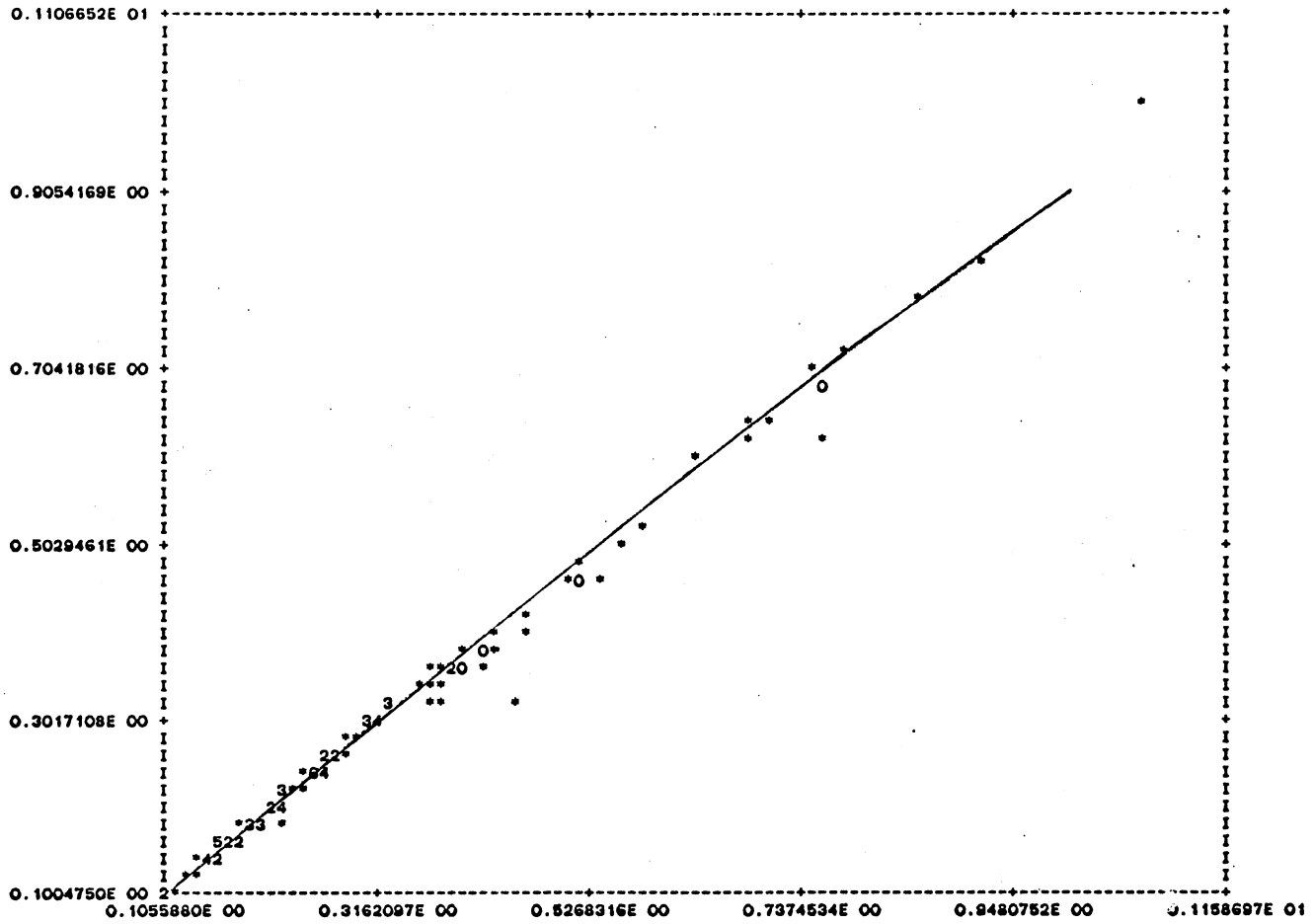

Figure 18. Substrate Utilization as a Function of Mass Substrate Loading

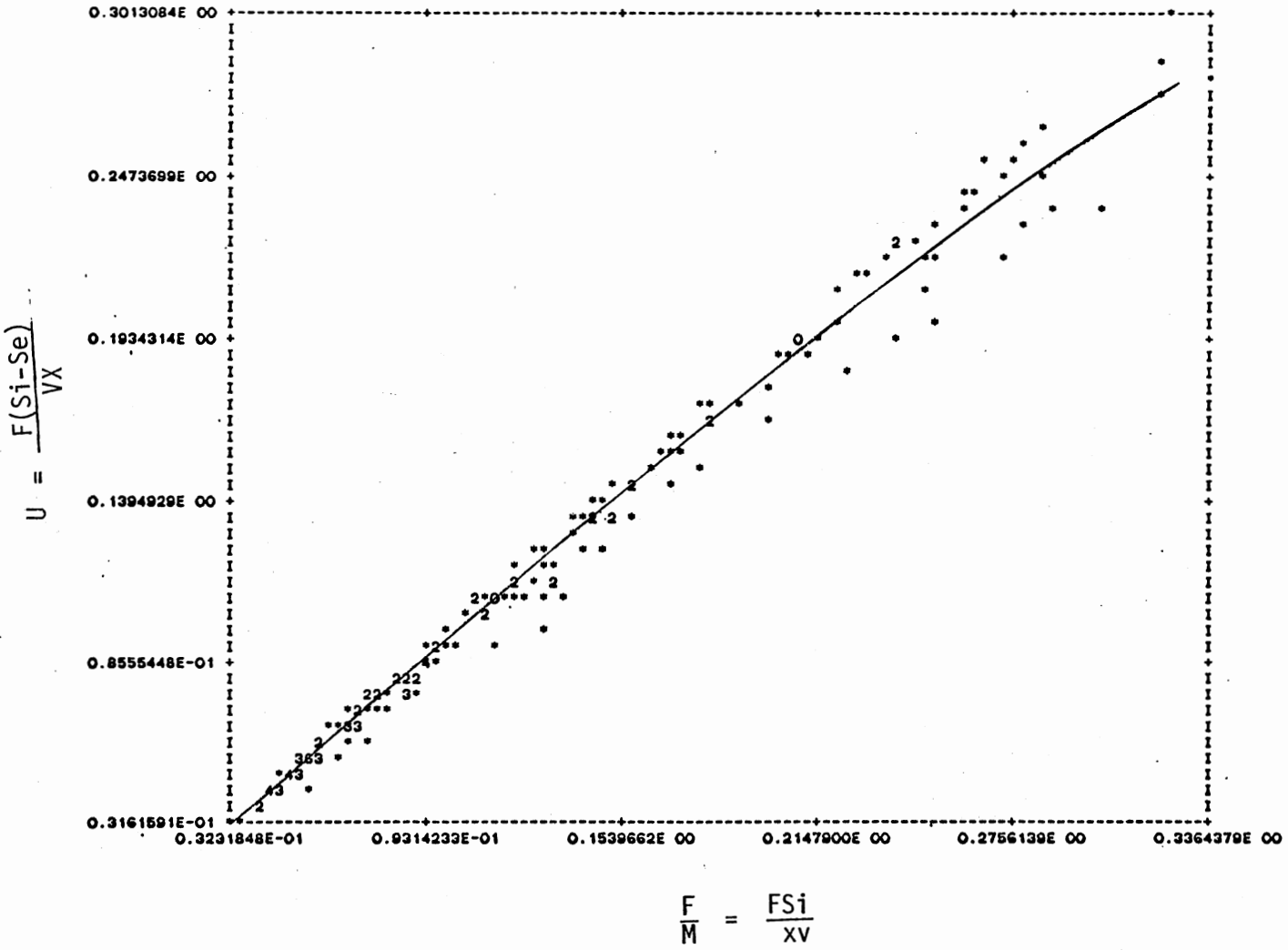

Figure 19. Substrate Utilization as a Function of Mass Substrate Loading in Terms of TOC

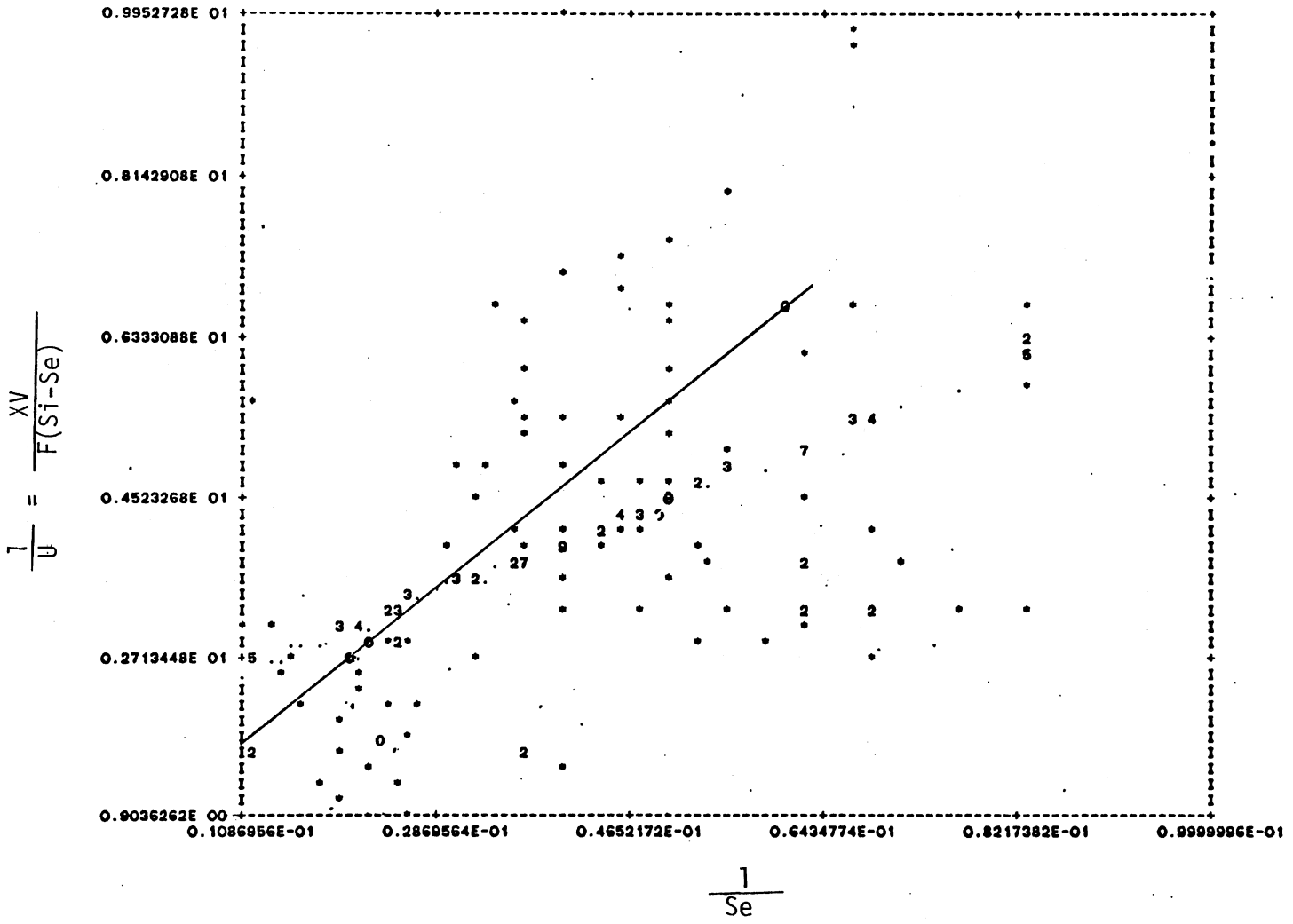

Figure 20. Graphical Determination of k and ks in Terms of COD

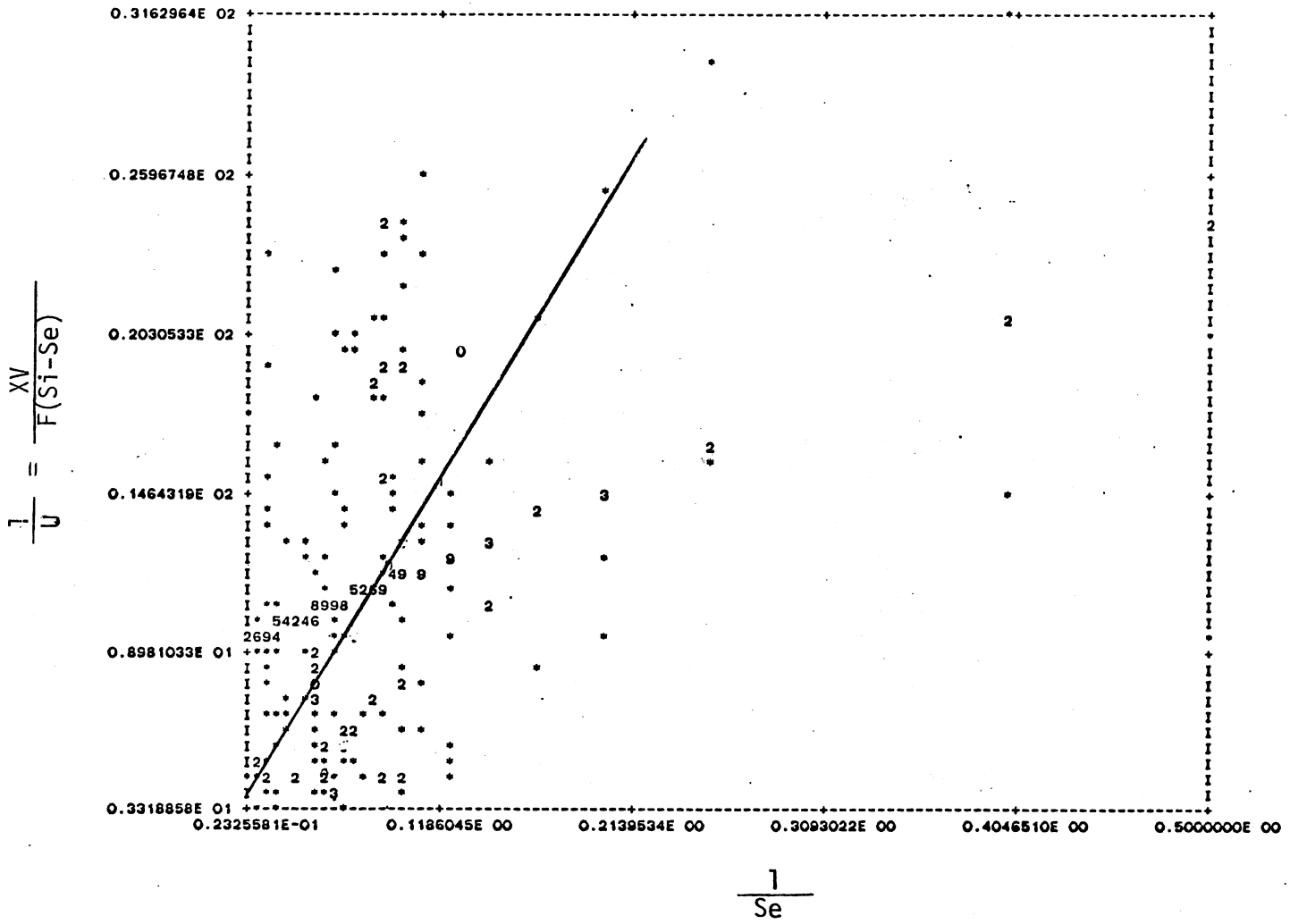

Figure 21. Graphical Determination of k and ks in Terms of TOC

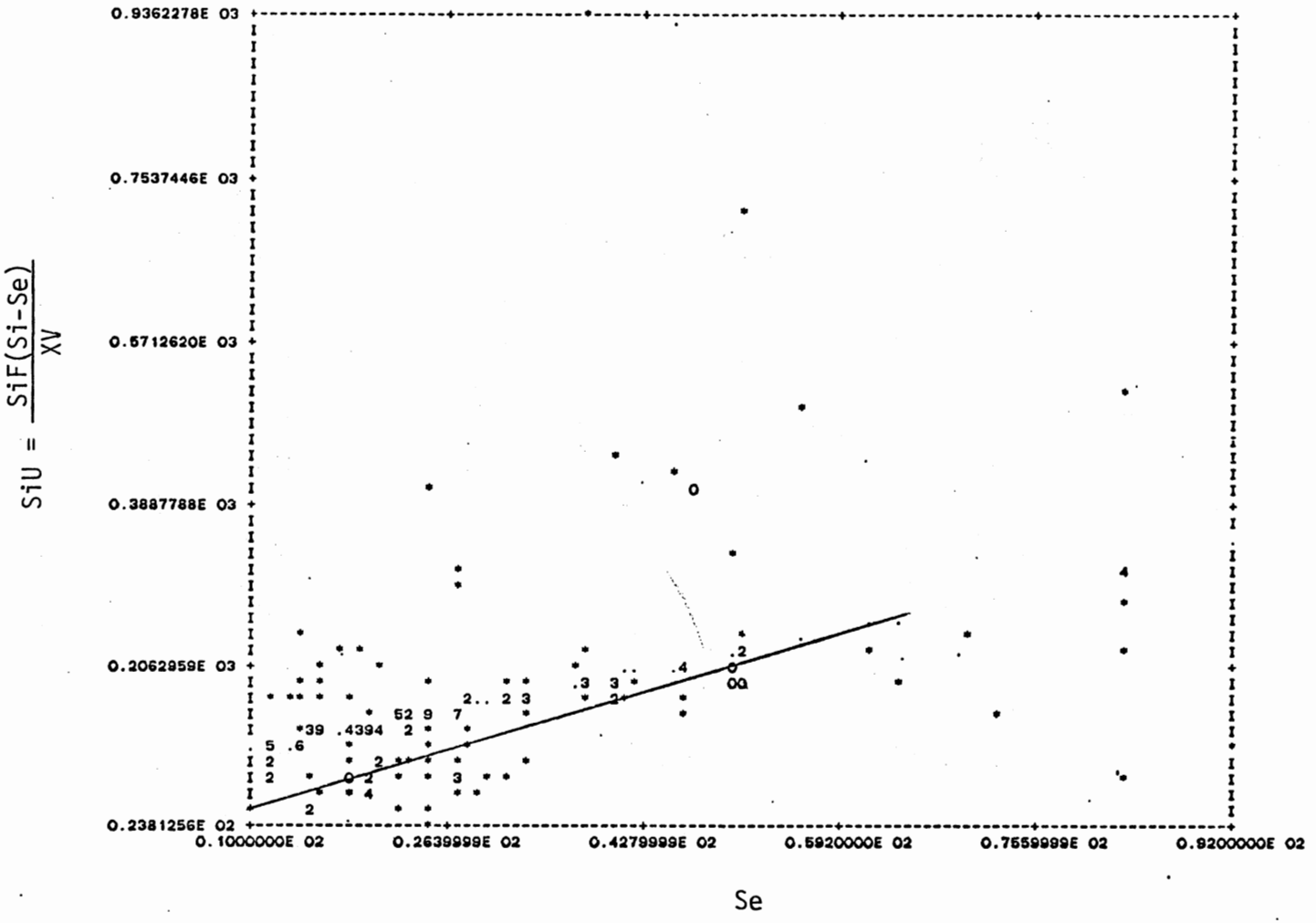

Figure 22. Graphical Determination of ke in Terms of COD

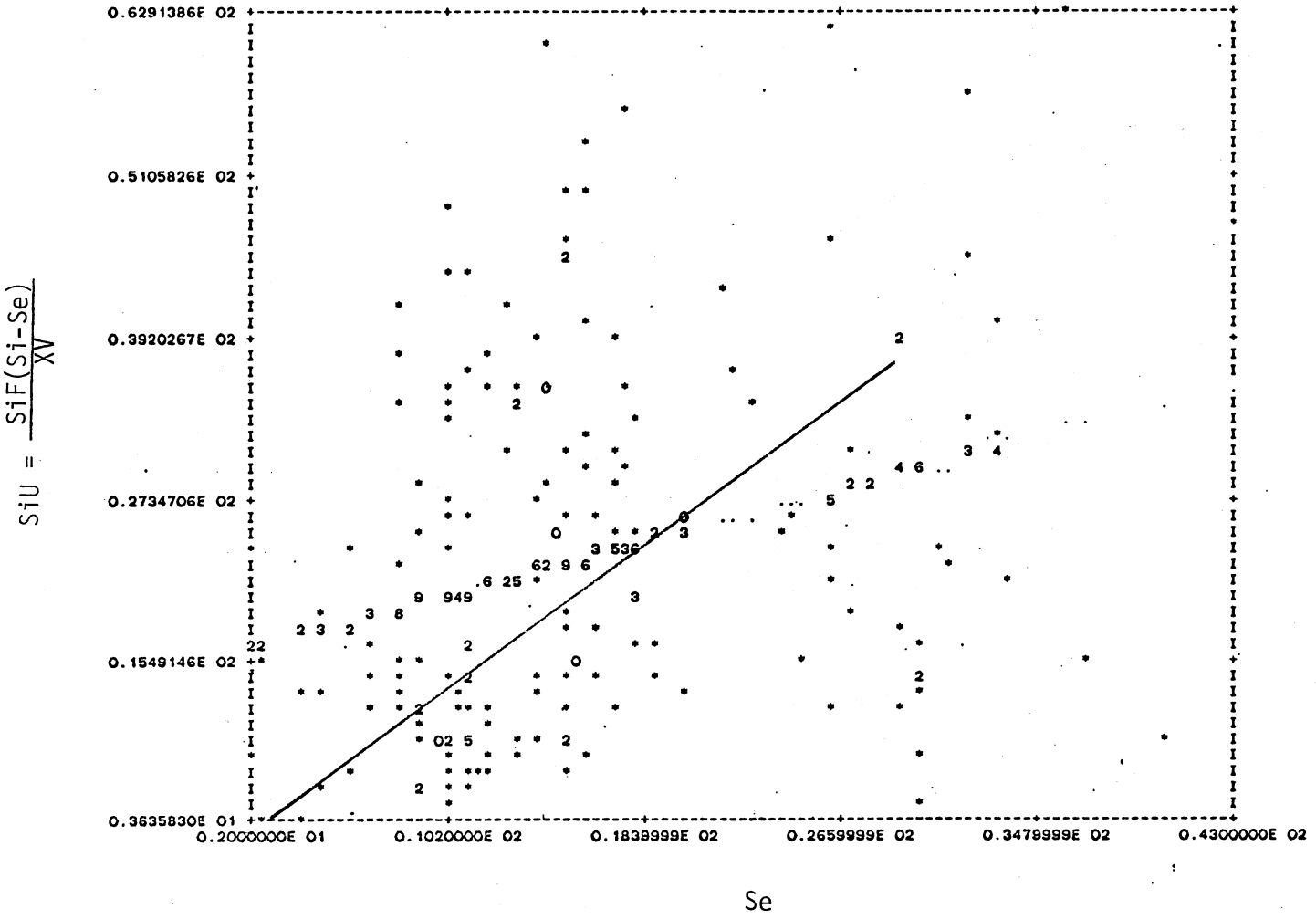

Figure 23. Graphical Determination of ke in Terms of TOC

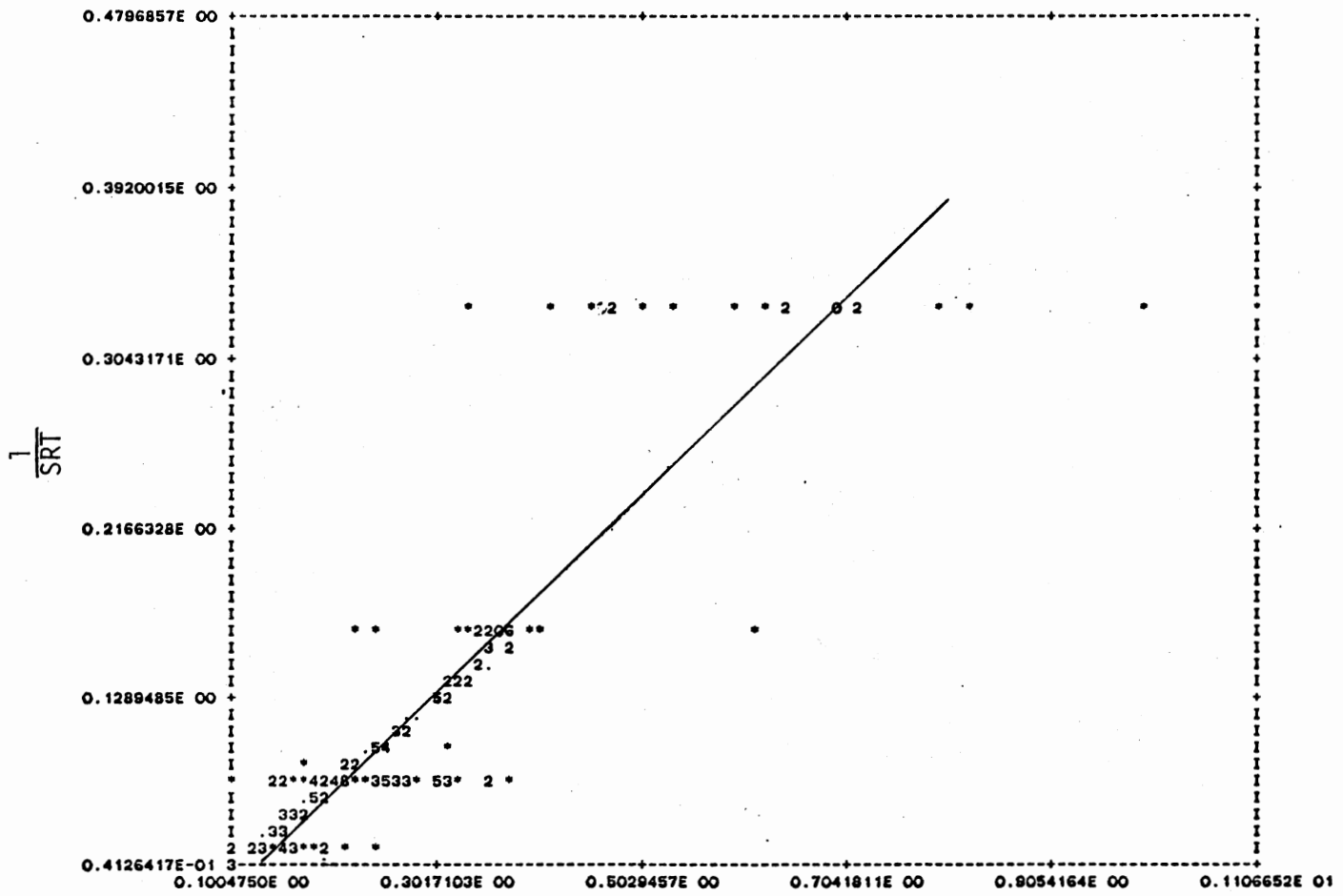

Figure 24. Graphical Determination of Y_t and k_d in Terms of COD

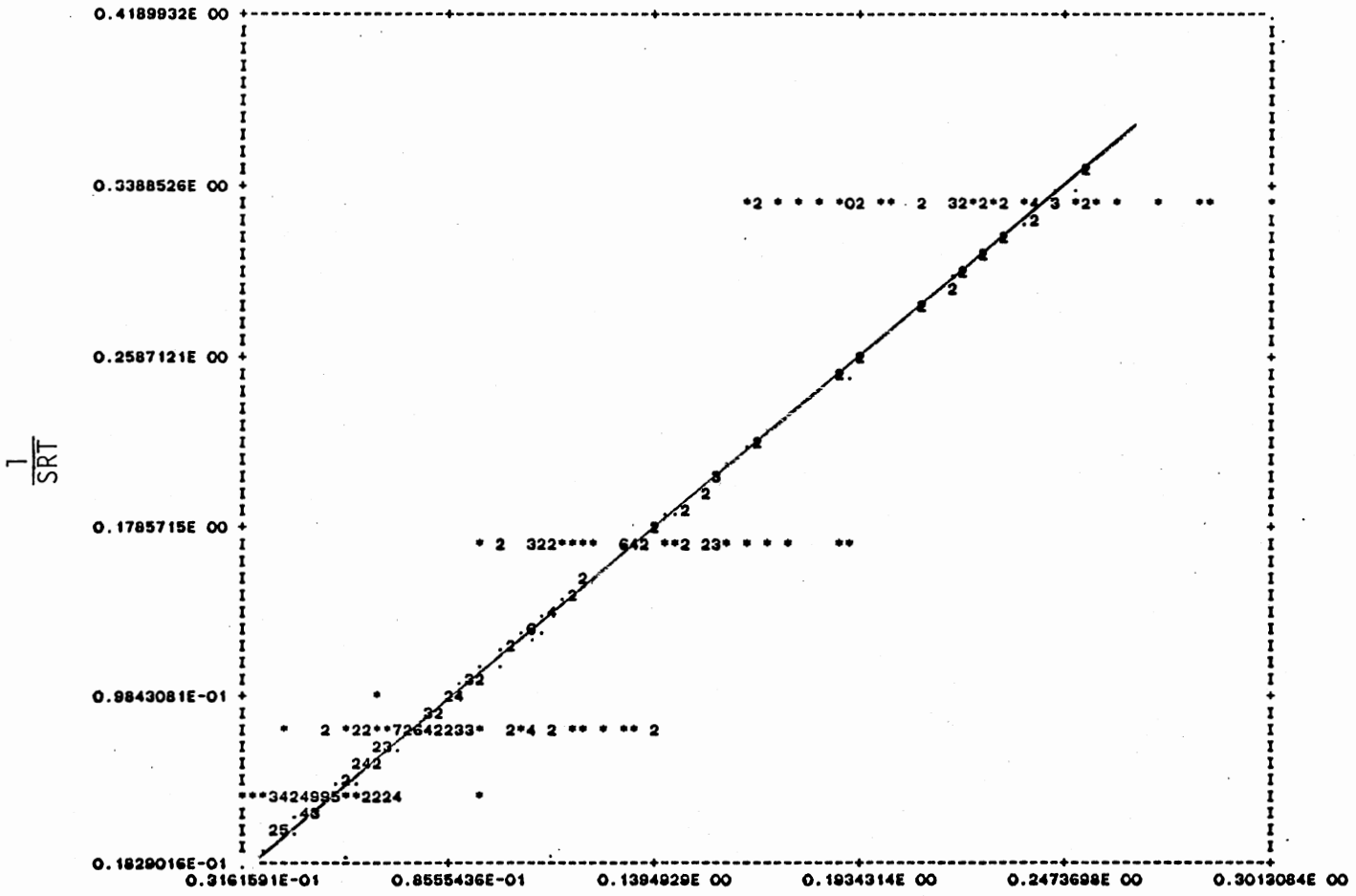

Figure 25. Graphical Determination of Y_t and k_d in Terms of TOC

utilization rate (U) against the reciprocal of food to microorganisms (F/M) after the Kincannon and Stover design model. The slope of the line is $\frac{k_B}{U_{max}}$ and the intercept of Y-axis is $\frac{1}{U_{max}}$. As seen in Figures 18 and 19, the specific substrate utilization rate (U) is plotted as a function of the F/M ratio. As is observed in Figures 20 and 21, the reciprocal of substrate utilization rate (U) is plotted as a function of reciprocal of effluent substrate to calculate $k\left(\frac{1}{k}\right.$, intercept of Y-axis$\left.\right)$ and $ks\left(\frac{k_s}{k}\right.$, the slope of the line$\left.\right)$ after Lawrence and McCarty design model. To compute the biological constant ($k\acute{e}$) for the modified Eckenfelder model, S_iU (influent substrate times substrate utilization rate) is plotted versus effluent substrate (Se), and is presented in Figures 22 and 23. Determination of true cell yield Y_t, the slope of the line, and an endogenous decay coefficient k_d - Y-axis intercept, are shown in Figures 24 and 25.

An attempt was made to fit a line through the mean values for calculation of Y_t and k_d to approach a basis for equal judgment. It can be noted also that a great deal of data scatter existed in the modified Eckenfelder, and Lawrence and McCarty models. It was a difficult task to draw a line though all of the data points. Representatives of the various degrees of data scatter are presented in Figues 20 through 25. The same kind of scatter was observed by the author on other research projects conducted in the Bioenvironmental Engineering Laboratories at Oklahoma State University. A model recently proposed by Kincannon and Stover deals with data scatter in detail. Examples of such plots, which eliminate the data scatter considerably, are seen in Figures 16 and 17.

A particular heavy metal could conceivably impact the values of

the biokinetic constants of a given wastewater. This impact could possibly be magnified by increasing concentrations of the metal. Of course, the data scatter can also be considered as a factor which could cause a change in the reported values of k, ks, and $k\acute{e}$.

Biokinetic Constants for Lead-fed Units

Table XVI presents the biokinetic constants (in terms of COD and TOC) obtained from the system which received lead at two different concentrations. It can be seen in Table XVI that values of k_B and U_{max} in terms of COD were higher for the control system. The system which received lead at a dosage of 0.56 mg/l had the lowest values for k_B and U_{max} in terms of COD. As the lead dosage increased further, the k_B and U_{max} values increased. This indicates a probable change in species predominance of the biomass system. The true cell yield (Y_t) increased with increasing lead dosages and was highest at a lead dosage of 3.32 mg/l. Other biokinetic constants (k_d, $k\acute{e}$, k, and k_s) also changed upon the addition of lead, though the changes in biokinetic constants did not follow any pattern of increase or decrease as the lead dosage increased. This clearly indicates that ecological changes are taking place in the system in response to increaes in lead concentration.

Biokinetic Constants for Zinc-fed Units

A summary of the biokinetic constants which describe the microorganisms subjected to the synthetic wastewater consisting of zinc at concentrations of 1.14 and 4.43 mg/l can be observed in Table XVII. It was found that k_B and U_{max} (with respect to COD) increased as zinc concentrations increased. k_B and U_{max} values in terms of TOC were lower

TABLE XVI

BIOKINETIC CONSTANTS FOR LEAD-FED UNITS

	COD							TOC						
Influent Lead mg/l	k_B day^{-1}	U_{max} day^{-1}	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s mg/l	k_B day^{-1}	U_{max} day^{-1}	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s day^{-1}
Control	12.03	11.58	0.26	0.51	4.2	1.53	155.50	2.79	2.65	0.03	1.48	1.36	1.04	123.04
0.56	3.56	3.39	0.02	0.61	3.70	0.71	44.05	4.25	3.12	0.14	1.97	0.92	0.30	7.85
3.32	7.03	6.77	0.01	0.97	3.88	2.06	245.34	1.96	1.86	0.06	1.61	1.58	2.05	444.64

TABLE XVII

BIOKINETIC CONSTANTS FOR ZINC-FED UNIT

Influent Zinc mg/l	COD							TOC						
	k_B day^{-1}	U_{max} day^{-1}	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s mg/l	k_B day^{-1}	U_{max} day-1	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s mg/l
Control	12.03	11.58	0.03	0.51	4.20	1.53	155.50	2.79	2.65	0.03	1.48	1.36	1.04	123.04
1.14	17.41	16.66	0.18	0.46	4.74	0.54	18.10	7.57	7.12	0.12	1.55	2.30	2.30	3.26
4.43	53.40	49.50	0.03	0.55	4.37	3.64	309.60	7.50	6.86	0.31	1.47	0.99	0.99	105.74

for the control system as compared to the system receiving zinc. However, among the systems which received zinc at dosages of 1.14 and 4.43 mg/l, there was not much difference between the k_B and U_{max} values, in terms of TOC. Values of true cell yield (Y_t) were not affected by the addition of 1.14 and 4.43 mg/l zinc. Values of decay coefficient (k_d), in terms of TOC, increased as zinc dosages increased. A notable increase in k_d (in terms of COD) occurred at a zinc dosage of 1.14 mg/l. When zinc concentrations increased from 1.14 to 4.43 mg/l, it caused k and k_s (in terms of COD) to increase from 0.54 to 3.64, and 18.10 to 309.60, respectively. The k and k_s values did not follow any particular trend when zinc at two different concentrations were added. $k\acute{e}$ values, in terms of COD, did not change appreciably as zinc dosages of 1.14 and 4.43 mg/l were added. $k\acute{e}$ values, in terms of TOC, decreased as zinc concentrations were increased from 1.14 to 4.43.

Biokinetic Constants for Cadmium-fed Units

Table XVIII summarizes the results of the biokinetic constants plots for the units which received the four different concentrations of cadmium. Generally, the addition of cadmium at various concentrations generated lower values of U_{max} and k_B, in terms of COD, compared with the control values. The values of k_B and U_{max}, in terms of TOC, were higher at cadmium concentrations of 1.27 and 9.67 than control values. The decay coefficient (k_d) value ranged between 0.01 and 0.07 when cadmium was administered to the system. Values of the true cell yield (Y_t), in terms of COD and TOC, were altered slightly in comparison with control values except at the dosage of 6.02 mg/l, at which point the Y_t, based on COD, was 0.91, which was much higher than the control value.

TABLE XVIII

BIOKINETIC CONSTANTS FOR CADMIUM-FED UNITS

Influent Cadmium mg/l	COD							TOC						
	k_B day^{-1}	U_{max} day^{-1}	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s mg/l	k_B day^{-1}	U_{max} day^{-1}	k_d day^{-1}	Y_t	k'_e day^{-1}	k day^{-1}	k_s mg/l
Control	12.03	11.58	0.03	0.51	4.2	1.53	155.50	2.79	2.65	0.03	1.48	1.36	1.04	123.04
1.27	8.37	8.99	0.04	0.76	2.99	1.51	177.18	5.90	6.21	0.00	1.24	2.39	0.76	48.18
4.06	3.08	3.10	0.07	0.78	4.18	0.97	82.87	2.05	1.97	0.04	1.52	5.21	0.26	27.02
6.02	2.95	2.96	0.06	0.91	3.63	1.54	187.83	1.43	1.40	0.02	1.77	1.81	1.13	159.27
9.67	4.21	4.13	0.01	0.54	7.51	5.39	831.88	8.55	7.89	0.01	1.45	1.87	0.85	192.00

Values of k, in terms of TOC, were reduced as cadmium concentration increased except at 6.02 mg/l, which was somewhat higher than the control value. Generally, values of k and ks (in terms of TOC and COD) determined for activated sludge systems exposed to 9.67 mg/l influent cadmium concentrations were significantly different from those of the control unit. An exception would be the k value (in terms of TOC) determined at the 9.67 mg/l influent cadmium concentration. The most significant effect of cadmium on $k\acute{e}$, in terms of TOC, occurred at a dosage of 4.06 mg/l. It seems that different concentrations of cadmium caused changes in all constants, but did not follow any regular pattern.

Heavy Metal Removal

Lead concentrations in the influent, effluent, and sludge for activated sludge systems operated at 3, 6, and 12 day SRT's are shown in Figures 26 to 28, respectively. Figure 26 describes the influent and effluent lead concentrations and lead uptake by MLSS at 3 day SRT.

At the influent concentration of 0.56 mg/l, the effluent soluble lead concentration was within a range of 0.05 and 0.11 mg/l. When the influent lead dosage was increased to 3.32 mg/l, the effluent soluble lead concentration immediately jumped to a level of 0.33 mg/l. This was followed by a rather fast rate of decrease in the effluent soluble lead concentration and finally stabilized at 0.05 mg/l. The same trend was observed for higher dosages also. When the influent lead concentration was increased to 5.46 mg/l, the effluent soluble lead concentration immediately peaked to a value of 0.32 mg/l, followed by a gradual decrease, and finally stabilized at 0.07 mg/l. The effluent soluble lead concentration peaked at a value of 0.47 mg/l for a lead dosage of

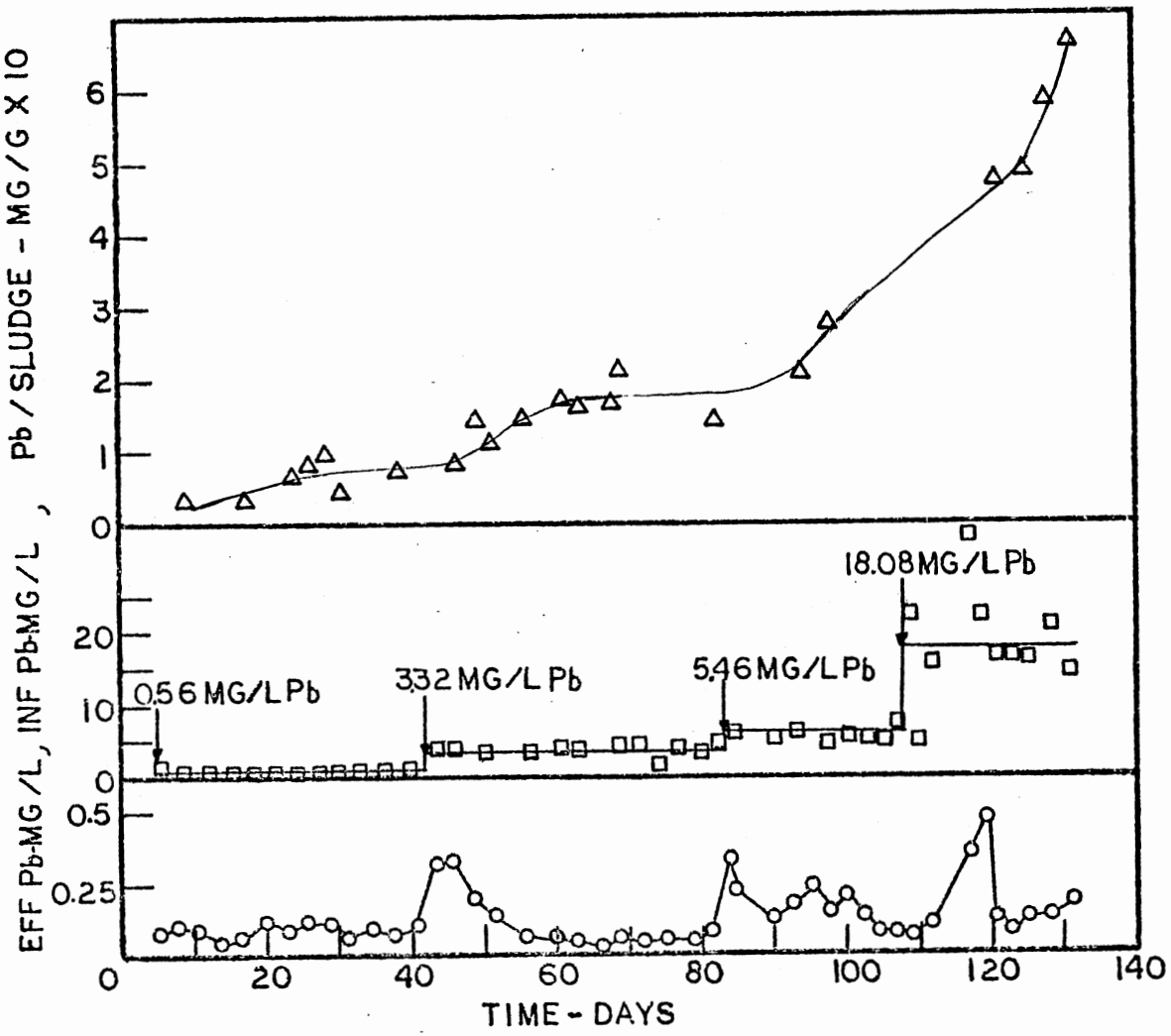

Figure 26. Influent Lead, Effluent Soluble Lead and Lead Uptake by the Activated Sludge Unit Operated at an SRT of 3 days

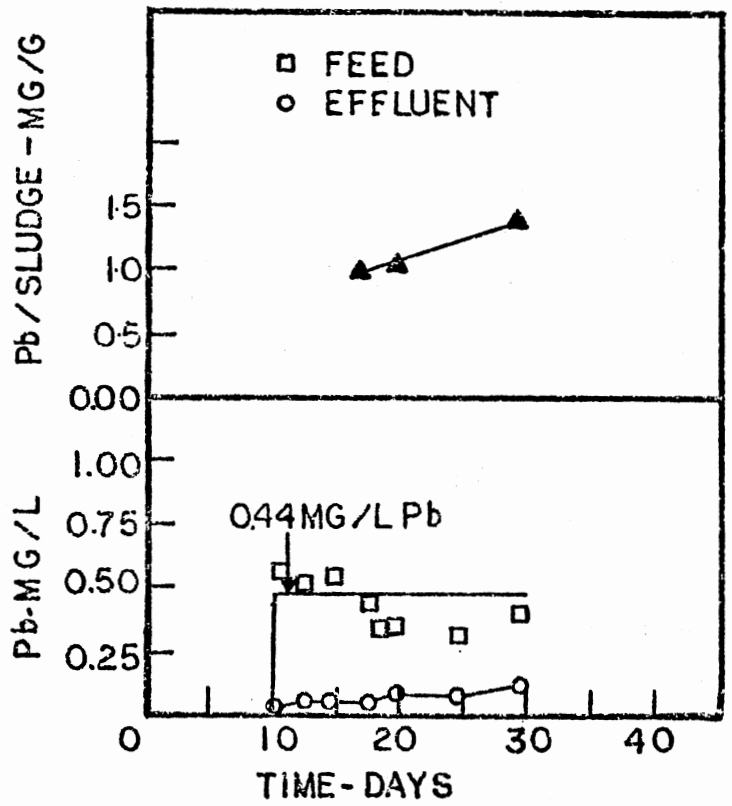

Figure 27. Influent Lead, Effluent Soluble Lead and Lead Uptake by the Activated Sludge Unit Operated at an SRT of 6 days

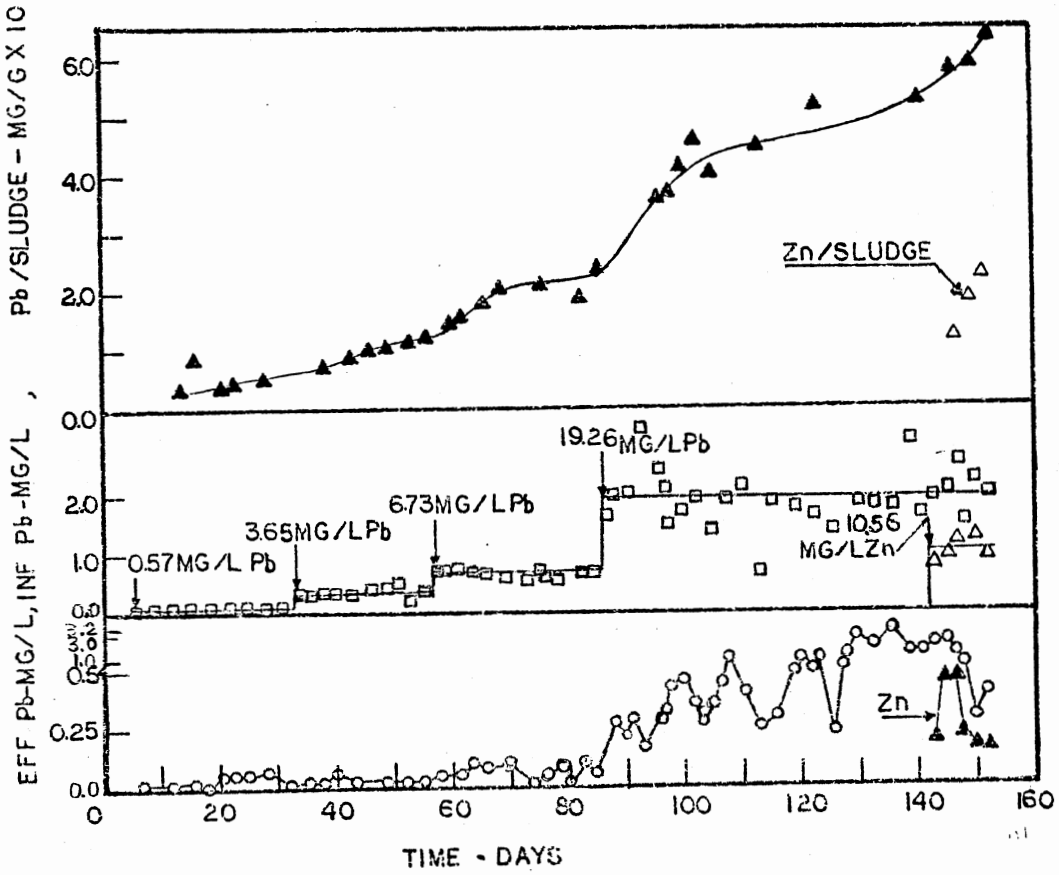

Figure 28. Influent Lead, Effluent Soluble Lead and Lead Uptake by the Activated Sludge Unit Operated at an SRT of 12 days

18.08 mg/l, which is rather high compared to the peak values attained for previous dosings. However, the effluent soluble lead concentration after the system stabilized was 0.12 mg/l, which is higher than other dosages. The above results indicate that the biomass had a considerable capacity for lead uptake. However, it could not cope with the sudden increase in influent concentrations. This is substantiated by the sludge concentration levels of 7.50, 18.0, 28.0, and 66.5 mg/l lead per gram dry weight of sludge when the system received the lead dosages of 0.56, 3.32, 5.46, and 18.08 mg/l, respectively. Even at the constant influent lead dosage, the sludge lead concentration showed a continued increase of lead in the sludge. Whenever the influent lead concentration was increased there was a steep increase in the sludge lead concentration. A rapid phase of lead uptake which is followed by a slower uptake at lead dosages of 0.56 and 3.32 mg/l can be seen in Figure 26.

Figure 27 shows effluent characteristics in terms of soluble lead as well as the lead accumulation in the biomass and influent lead dosages for the 6 day SRT unit. When the lead dosage of 0.44 mg/l was applied to the system, the effluent soluble lead concentration ranged between 0.03 and 0.11 mg/l. The sludge lead concentration was 1.0 mg lead per gram dry weight of sludge and gradually increased and reached a value of 1.4 mg lead per gram dry weight of sludge.

Figure 28 depicts the effluent and influent lead concentrations and lead uptake by sludge at 12 day SRT. When the 12 day SRT unit was subjected to the initial lead dosage of 0.57 mg/l, the effluent soluble lead concentration was rather steady and ranged between 0.01 and 0.06 mg/l. When the lead dosage was increased to 3.65 mg/l, there was no change in the effluent soluble lead concentration compared with the

previous dosage. The effluent soluble lead concentration ranged between 0.01 and 0.04 mg/l (averaging 0.02 mg/l). The same trend was observed even for the next higher dosage level of 6.73 mg/l. The effluent soluble lead concentration at this dosage was between 0.01 and 0.10 mg/l, with an average of 0.06 mg/l. However, when the influent lead concentration was further increased to a dosage of 19.26 mg/l, it resulted in a high leakage of lead in the effluent, which fluctuated considerably. The effluent soluble lead concentration at this dosage ranged between 0.15 and 3.21 mg/l, with an average of 0.86 mg/l.

In summary, the effluent soluble lead concentration was independent of influent soluble lead concentrations up to 6.73 mg/l, and effluent with high concentrations of lead were not produced until the system was exposed to a lead dosage of 19.26 mg/l. Results presented in Figure 28 show that the biomass had considerable amount of metal uptake capacity for lead and could cope with the sudden increase in influent dosages up to 19.26 mg/l.

Throughout this run, even at a constant lead dosage, the sludge lead concentration showed a gradual increase. Whenever the influent concentration was increased, there was a relatively steep increase in the sludge lead concentration. A rapid phase of lead uptake which is followed by a slower uptake is very obvious at a lead dosage of 6.73 mg/l. For influent lead concentrations of 0.57, 3.65, 6.73, and 19.26 mg/l, sludge lead concentrations reached levels of 5.0, 12.0, 21.0, and 65.0 mg lead per gram dry weight of sludge, respectively.

Table XIX summarizes the operating characteristics (in terms of lead) of the units that received various lead dosages at different solids retention times (3, 6, and 12 day). It was found that metal removals

TABLE XIX

LEAD REMOVAL EFFICIENCIES

		SRT = 3 days				SRT = 6 days	SRT = 12 days			
		Influent Lead (Pb) (mg/l)				Influent Lead (Pb) (mg/l)	Influent Lead (Pb) (mg/l)			
		0.56	3.32	5.46	18.08	0.44	0.57	3.65	6.73	19.26
Heavy Metal Removal	N	18	18	10	10	8	11	12	14	31
	Range	0.05-0.11	0.03-0.11	0.07-0.32	0.05-0.47	0.03-0.11	0.01-0.06	0.01-0.04	0.01-0.10	0.15-3.21
Soluble Effluent (mg/l)	Mean	0.08	0.10	0.18	0.16	0.07	0.02	0.02	0.06	0.86
	S.D.	0.02	0.10	0.07	0.14	0.02	0.02	0.01	0.03	0.87
Removal Efficiency %		85.7	97.0	96.7	99.1	84.1	96.5	99.4	99.1	95.5

were 85.7%, 97.0%, 96.7%, and 99.1% at lead concentrations of 0.56, 3.32, 5.46, and 18.08 mg/l, respectively, for the 3 day SRT. Effluent soluble lead increased slightly as feed lead dosages increased up to 18.08 mg/l. It was seen that the 12 day SRT unit had better removal efficiency in terms of effluent soluble lead than the 3 and 6 day SRT units at influent lead concentrations of 0.57, 3.65, and 6.73 mg/l. The 3 day unit that received lead at 18.08 mg/l generated a higher lead removal efficiency than the 12 day reactor which was subjected to lead at 19.26 mg/l.

In general, better performance of systems at higher SRTs has been reported by other researchers. The higher the SRT, the higher will be the cell concentration and better the effluent quality. However, in this case, due to the continuous addition of lead, the accumulation of lead in the system was increasing. In the case of higher SRTs, new sludge production is less; therefore, the availability of cell capacity for further metal uptake was reduced. In addition to this, as shown in Figure 9, the biomass concentration of the higher SRT unit started to decrease, thereby decreasing the cell capacity for metal uptake. This could be a possible reason for higher concentration of lead in the effluent for the higher SRT (12 day) system. A metal removal efficiency of 84.1% was obtained when the unit was run at a 6 day SRT and a lead concentration of 0.44 mg/l.

Zinc Studies

The behavior of the activated sludge systems when receiving various zinc concentrations can be found in Figures 29 through 31. Figure 29 presents influent zinc, effluent soluble zinc and zinc uptake by the

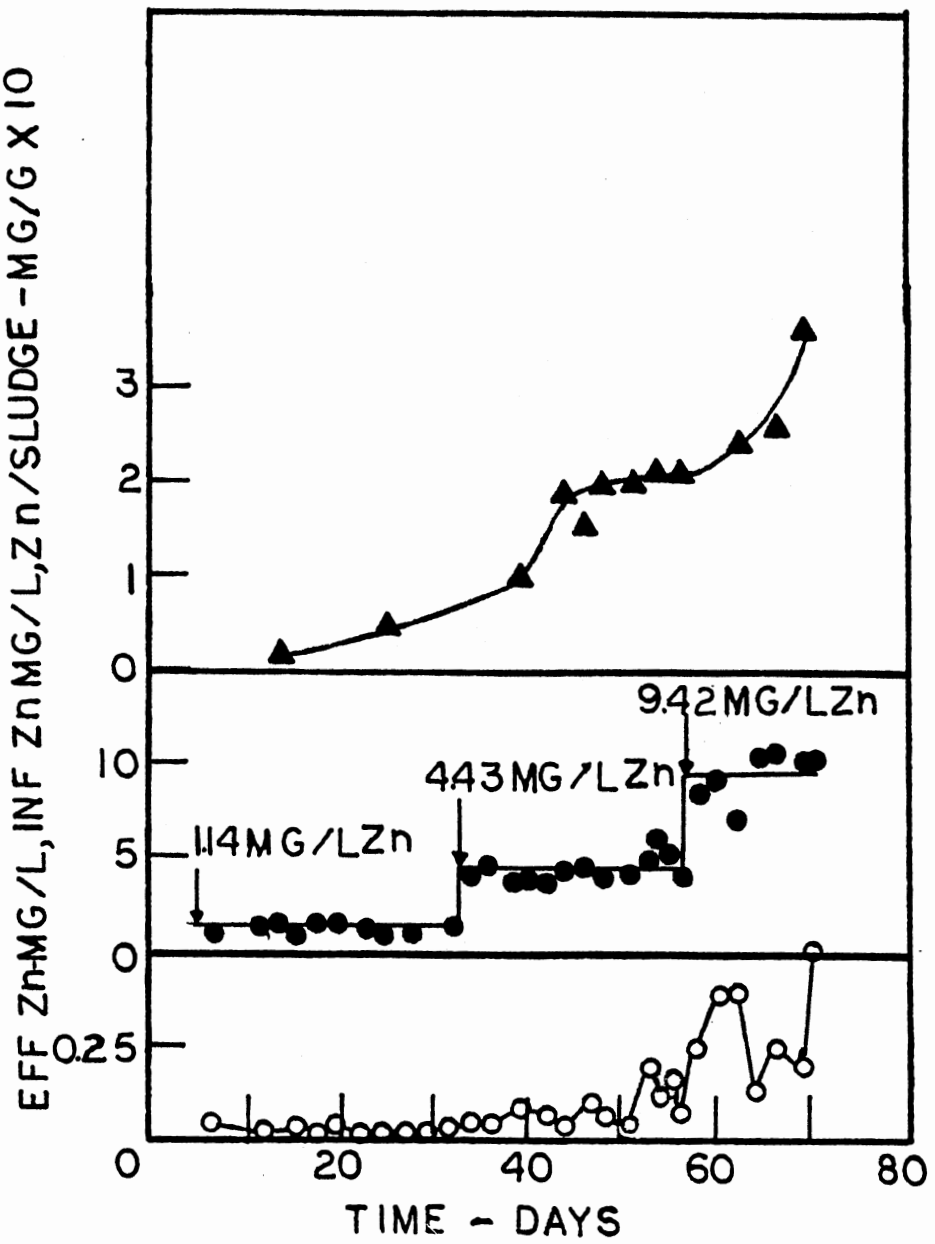

Figure 29. Influent Zinc, Effluent Soluble Zinc and Zinc Uptake by the Activated Sludge Unit Operated at an SRT of 3 Days

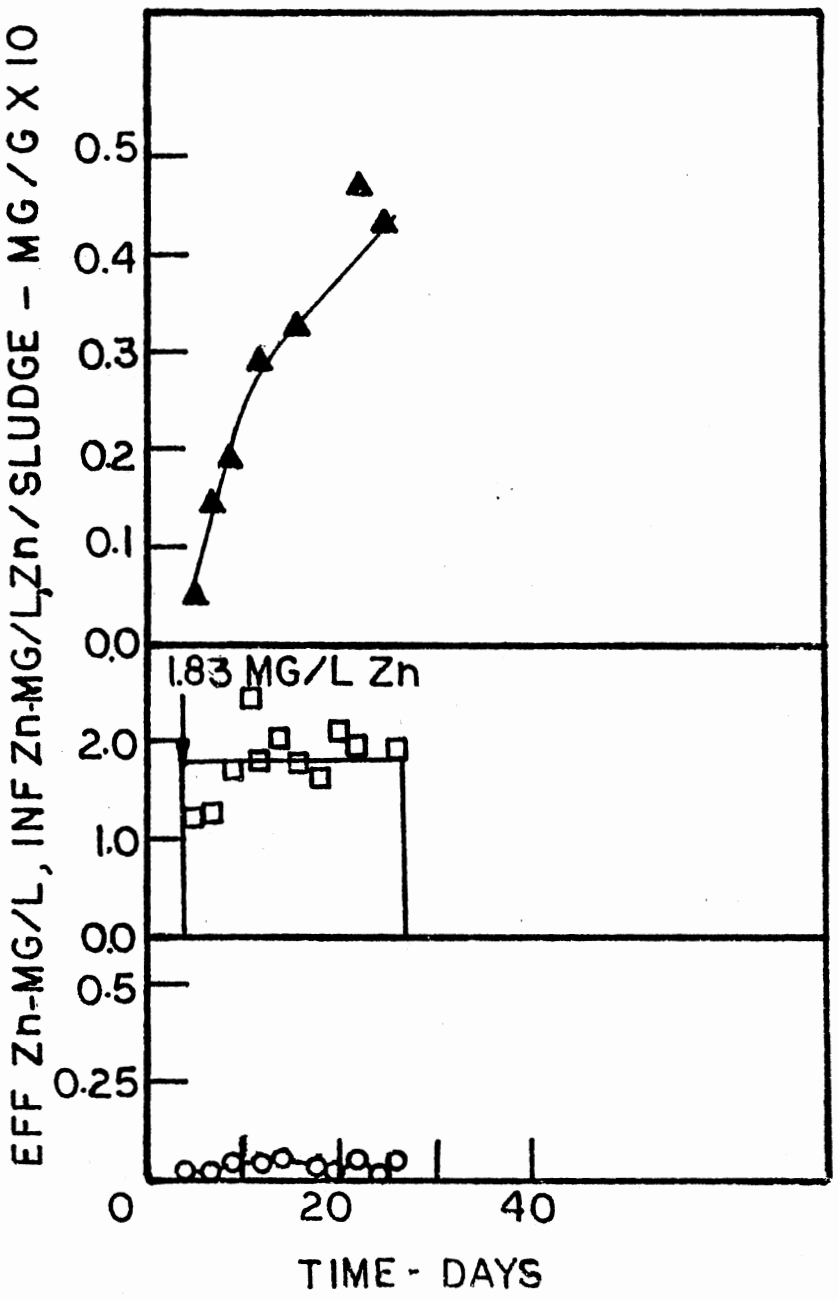

Figure 30. Influent Zinc, Effluent Soluble Zinc and Zinc Uptake by the Activated Sludge Unit Operated at an SRT of 6 Days

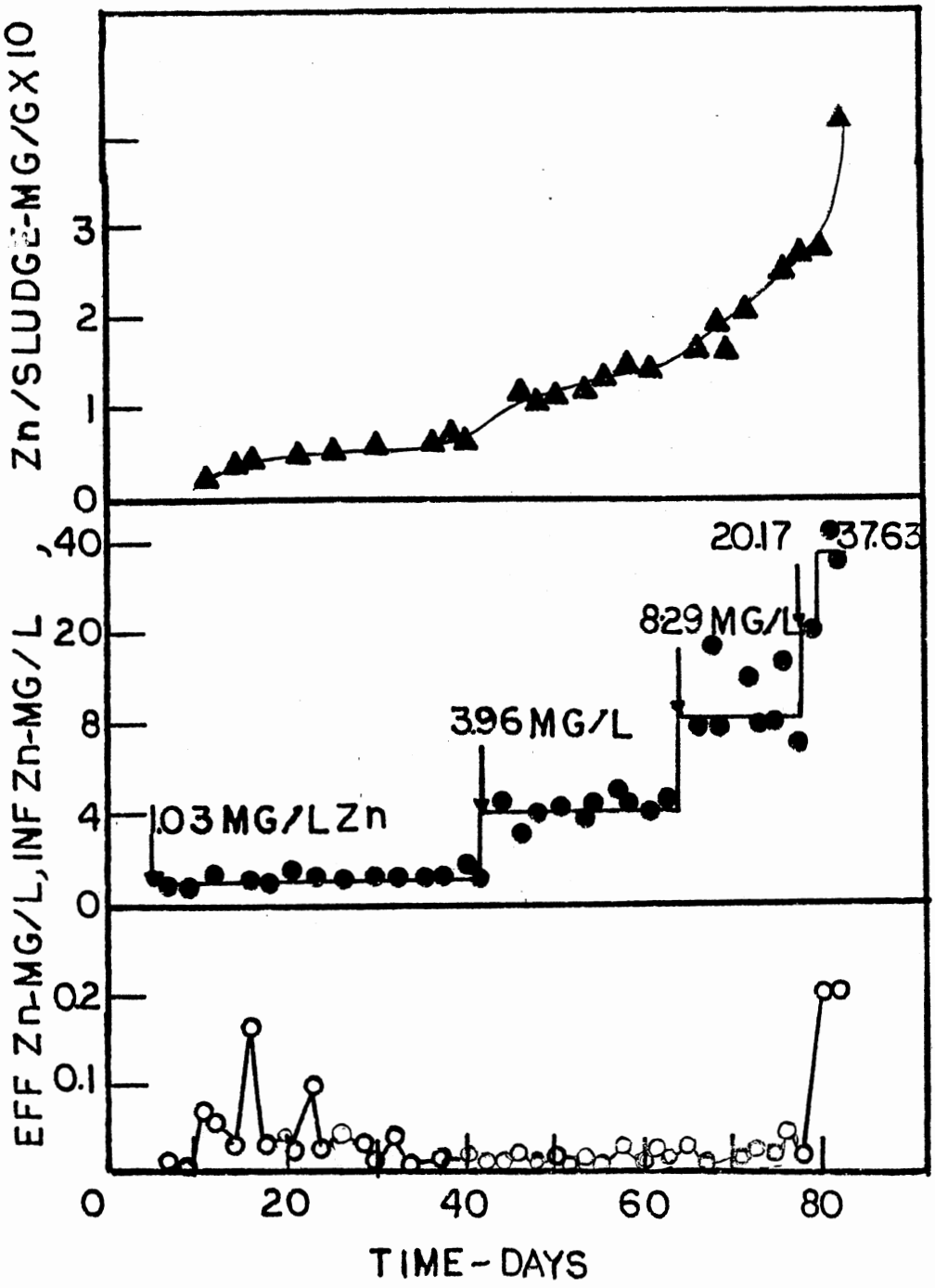

Table 31. Influent Zinc, Effluent Soluble Zinc and Zinc Uptake by the Activated Sludge Unit Operated at an SRT of 12 days

activated sludge unit operated at a 3 day SRT. It can be seen that when zinc at a dosage of 1.14 mg/l was added to the system, the effluent soluble zinc concentration was within a range of 0.02 and 0.06 mg/l (averaging 0.04 mg/l) without fluctuation. When the dosage was further increased to 4.43 mg/l, the effluent soluble zinc concentration was higher than the previous dosage and within a range of 0.04 and 0.21 mg/l (averaging 0.10 mg/l). In this case, the effluent concentration fluctuated and continued doing so during the next dosage of 9.42 mg/l also. The effluent soluble zinc concentration ranged between 0.12 and 0.50 mg/l, with an average of 0.30 mg/l, when the system received zinc at a dosage of 9.42 mg/l.

Zinc accumulation in the sludge increased continuously. The step increases in the influent zinc concentration changed the rate of increase in the sludge appreciably. Figure 29 shows two different rates of zinc uptake (a rapid uptake followed by a slower uptake) by the biomass at a zinc dosage of 4.43 mg/l. At this dosage, the sludge zinc concentration reached an equilibrium level of 20.0 mg zinc per gram dry weight of sludge. For influent zinc dosages of 1.14 and 9.42 mg/l, sludge zinc concentrations attained levels of 5.0 and 36.0 mg zinc per gram dry weight of sludge, respectively.

Zinc at a concentration of 1.83 mg/l was introduced to the reactor operating at a 6 day SRT. The fate of zinc in this case is shown in Figure 30. A fairly uniform and low level of zinc in the effluent was generated (less than 0.05 mg/l) and ranged between 0.00 and 0.05 mg/l. The level of zinc uptake achieved by the biomass was 4.2 mg zinc per gm dry weight of sludge. The sludge zinc concentration showed a continuous increase throughout this run.

Effluent quality (in terms of soluble zinc) for the 12 day SRT unit subjected to six different concentrations of zinc is presented in Figure 31. Effluent soluble zinc concentrations fluctuated upon addition of 1.03 zinc ranging between 0.00 and 0.16 mg/l. The results indicate that the high level of zinc in the feed solution (3.96, 8.29, and 20.17 mg/l) did not cause any changes in the effluent soluble zinc except at a zinc concentration of 37.63 mg/l, which produced high effluent soluble concentrations of 0.2 mg/l, in comparison with lower influent dosates. For influent zinc concentrations of 1.03, 3.96, 8.29, and 37.63 mg/l, sludge zinc concentrations attained 5.5, 14.0, 22.5, and 41.5 mg zinc per gram dry weight of sludge, respectively. Figure 31 presents two different rates of zinc uptake by the biomass at a zinc dosage of 1.03 mg/l. A rapid uptake rate is followed by a slower rate as reported by other workers (36, 40). When the system was subjected to a step increase in zinc concentrations of 3.96 mg/l, the sludge zinc concentration showed a step increase up to day 50, followed by a rather gradual increase until the dosage was further increased.

The zinc removal efficiencies of the units which received various concentrations at different SRTś are shown in Table XX. Table XX shows that zinc removal efficiencies for the 3 day SRT of 96.5, 97.7, and 96.8 percent were achieved at influent zinc concentrations of 1.14, 4.43, and 9.42 mg/l, respectively. A zinc removal efficiency of 98.4 percent was obtained for the 6 day SRT unit. It was observed that for the 12 day SRT system, zinc removal efficiencies of 97.1, 99.7, 99.7, 99.8, and 99.5 percent were found when synthetic wastewaters containing zinc concentrations of 1.03, 3.96, 8.29, 20.17, and 37.63 mg/l, respectively, were added. The system with high SRTś (6 and 12 days) exhibited

TABLE XX

ZINC REMOVAL EFFICIENCIES

		SRT = 3 days			SRT = 6 days	SRT = 12 days				
		Influent Zinc (Zn) (mg/l)			Influent Zinc (Zn) (mg/l)	Influent Zinc (Zn) (mg/l)				
		1.14	4.43	9.42	1.83	1.03	3.96	8.29	20.17	37.63
Heavy Metal Removal	N	14	13	7	12	23	13	10	2	2
	Range	0.02-0.06	0.04-0.21	0.12-0.50	0.00-0.05	0.00-0.16	0.00-0.02	0.00-0.04	0.04-0.04	0.20-0.20
Soluble Effluent (mg/l)	Mean	0.04	0.10	0.30	0.03	0.03	0.01	0.02	0.04	0.20
	S.D.	0.01	0.05	0.14	0.02	0.04	0.01	0.01	0.00	0.00
Removal Efficiency %		96.5	97.7	96.8	98.4	97.1	99.7	99.7	99.8	99.5

better zinc removal efficiency compared to low SRT system (3 days).

Cadmium Studies

Influent, effluent, and sludge cadmium concentrations for units operated at different SRT's (3, 6, and 20 days) are shown in Figures 32 through 34, respectively.

Figure 32 represents the response of the 3 day SRT unit which received cadmium at concentrations of 4.06, 6.02, 9.67, and 21.60 mg/l. When the system was subjected to cadmium dosages of 4.06 mg/l and 6.02 mg/l, the effluent soluble cadmium concentration stayed rather steady and ranged between 0.15 and 0.46, and 0.12 and 0.22 mg/l, respectively. The effluent soluble cadmium concentration increased slightly and was within a range of 0.22 and 0.58 mg/l (averaging 0.36 mg/l) when the system was subjected to a cadmium dosage of 9.67 mg/l. There was only a slight fluctuation at this dosage level. When the dosage was increased to 21.60 mg/l, the effluent soluble cadmium concentration showed considerable fluctuation, though it seemed to stabilize toward the end of this run. The effluent soluble cadmium concentration ranged between 0.25 and 3.98 mg/l with an average of 1.12 mg/l.

Figure 32 shows a rapid phase of cadmium uptake, followed by a slower uptake at a cadmium dosage of 4.06 mg/l. The same trend was observed when the system was subjected to dosages of 6.02, 9.67, and 21.60 mg/l. The initial sludge accumulation rate was much higher at a dosage of 21.60 mg/l than when compared to other dosages. Followed by this steep increase, the cadmium concentration in the sludge reached an equilibrium value of 80.5 mg cadmium per gram dry weight of sludge. For influent cadmium concentrations of 4.06, 6.02, and 9.67 mg/l, sludge

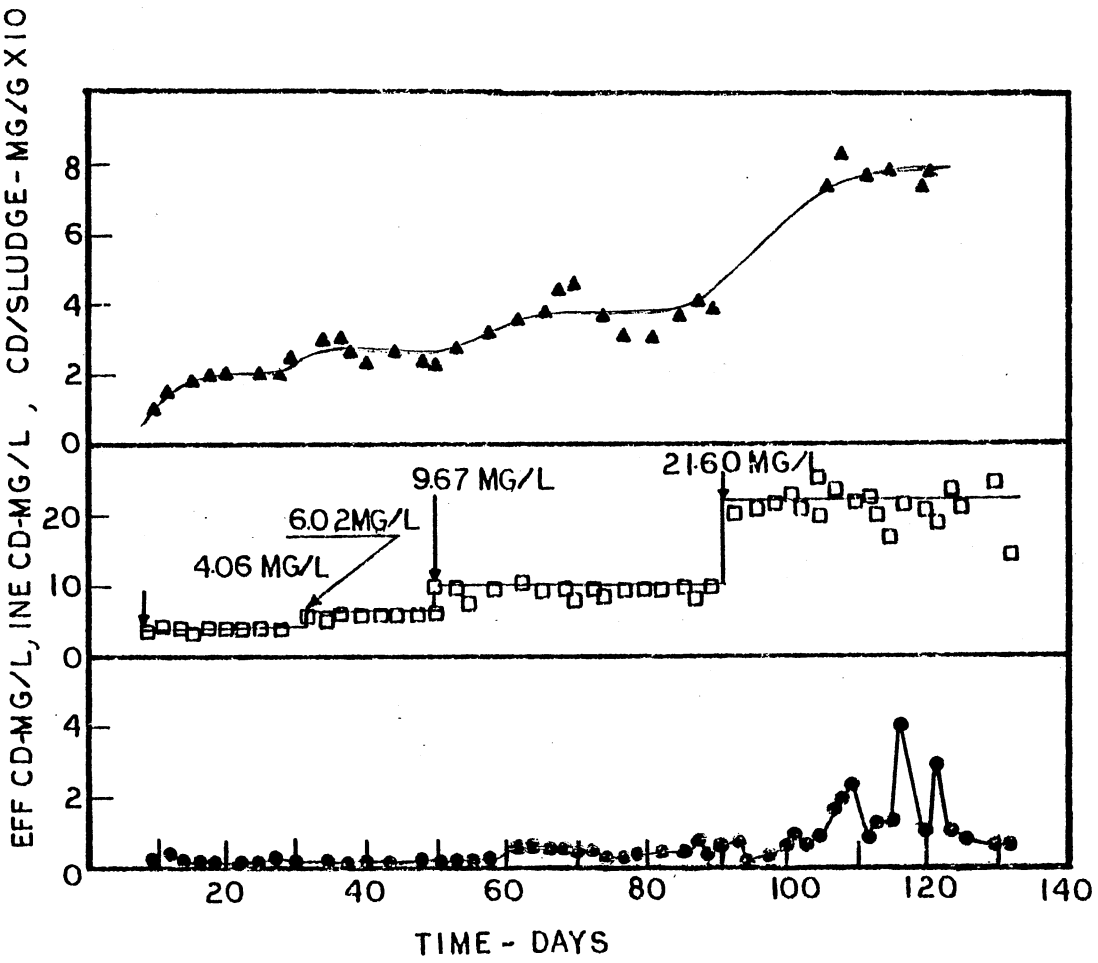

Figure 32. Influent Cadmium, Effluent Soluble Cadmium and Cadmium Uptake by the Activated Sludge Unit Operated at an SRT of 3 Days

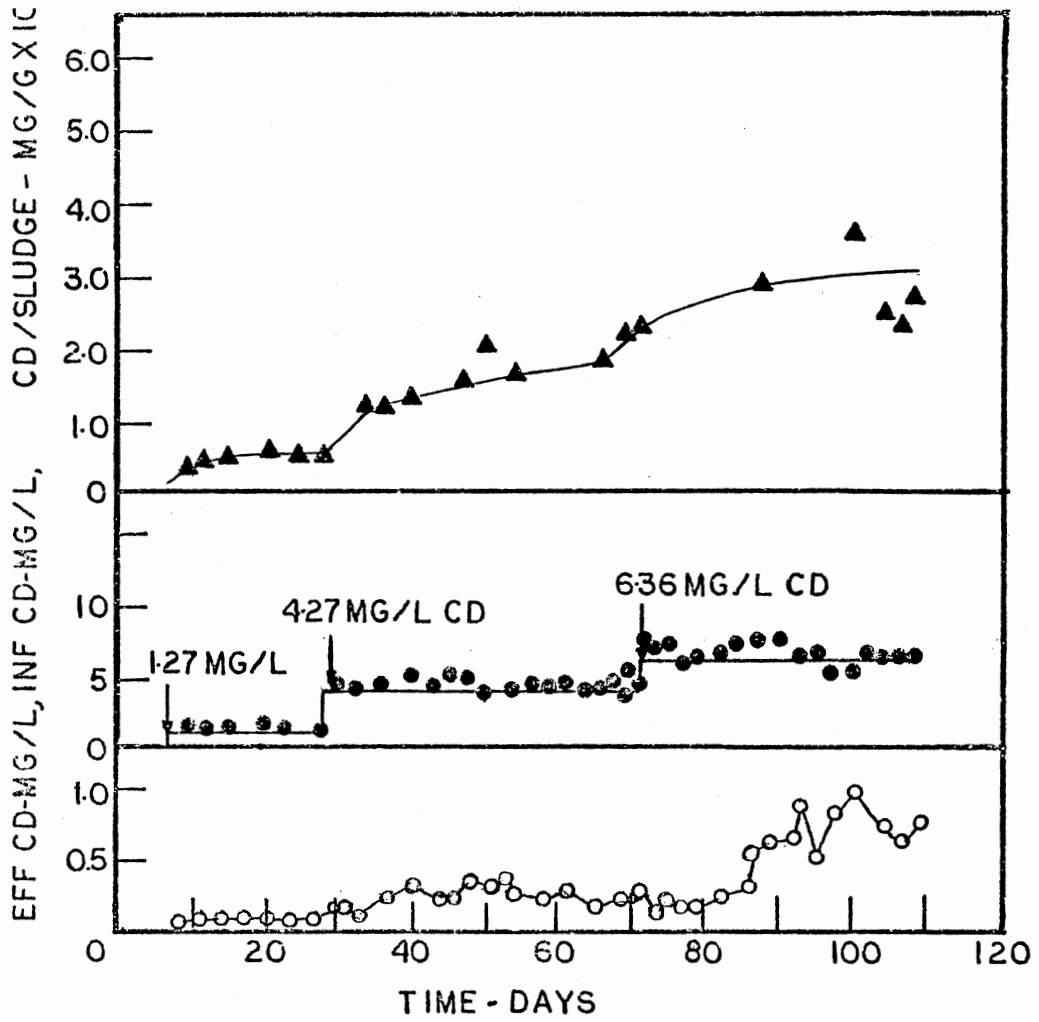

Figure 33. Influent Cadmium, Effluent Soluble Cadmium and Cadmium Uptake by the Activated Sludge Unit Operated at an SRT of 6 Days.

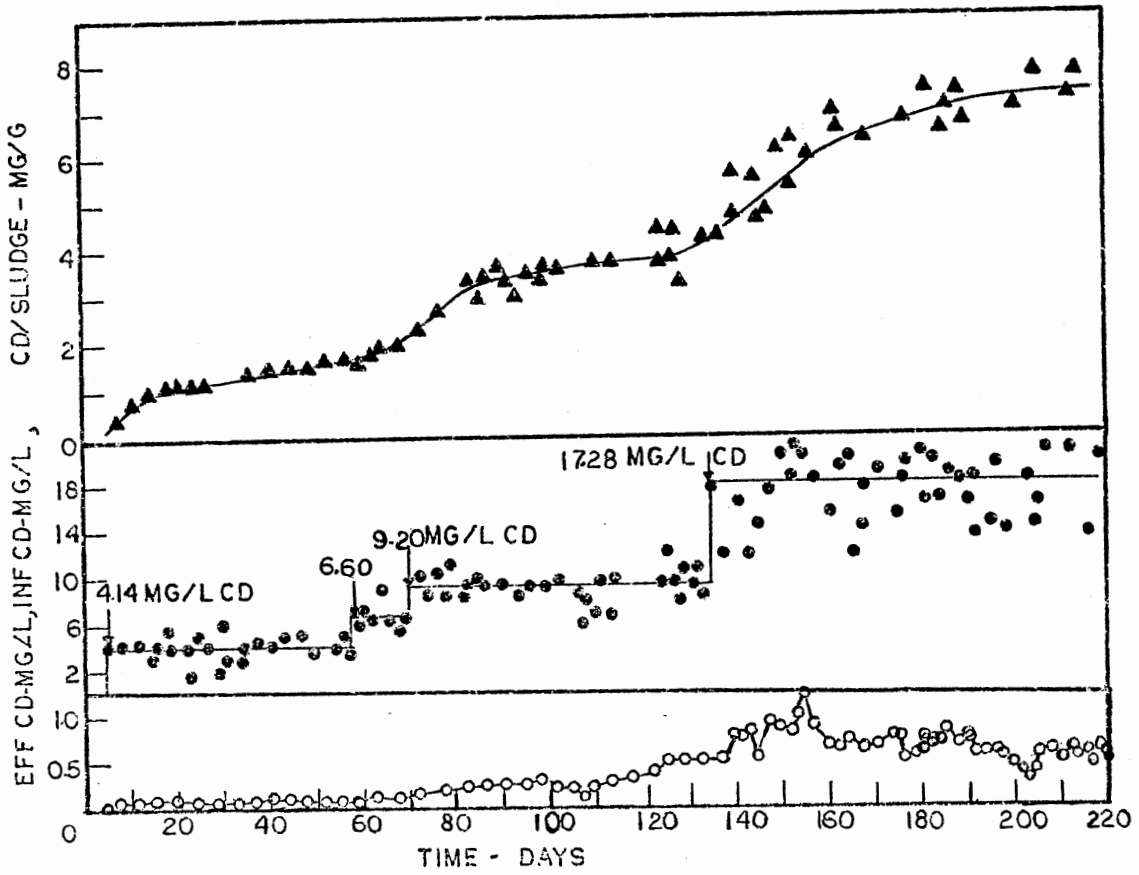

Figure 34. Influent Cadmium, Effluent Soluble Cadmium and Cadmium Uptake by the Activated Sludge Unit Operated at an SRT of 20 Days.

cadmium concentrations reached 20.0, 25.0, and 39.0 mg cadmium per gram dry weight of sludge, respectively.

Influent, soluble effluent, and sludge cadmium concentrations for the 6 day SRT unit have been depicted in Figure 33. The influent cadmium concentration of 1.27 mg/l produced low and uniform effluent soluble cadmium concentrations with an average of 0.06 mg/l. When the influent cadmium concentration was further increased to 4.27 mg/l, the effluent soluble cadmium concentration was higher than for the previous dosage and was within the range of 0.16 and 0.36 mg/l (averaging 0.24 mg/l). In this case, the effluent soluble cadmium concentration fluctuated considerably. When the influent soluble cadmium dosage was increased from 4.27 to 6.36 mg/l, the effluent soluble cadmium concentration showed a further increase and wider fluctuations. The effluent soluble cadmium concentration ranged between 0.14 and 0.93 mg/l, with an average of 0.50 mg/l.

Figure 33 shows a rapid phase of cadmium uptake which is followed by a slower uptake at a cadmium dosage of 1.27 mg/l. The same trend was observed when the system received cadmium at dosages of 4.27 and 6.36 mg/l. At a dosage of 6.36 mg/l, the cadmium concentration in the sludge reached an equilibrium level of 30.0 mg cadmium per gram dry weight of sludge. For influent cadmium concentrations of 1.27 and 4.27 mg/l, sludge cadmium concentrations reached 5.5 and 19.0 mg cadmium per dry weight of sludge, respectively.

Figure 34 shows the results that were obtained from the 20 day SRT reactor which was exposed to various cadmium dosages. When the system was subjected to a cadmium dosage of 4.14 mg/l, the effluent soluble cadmium concentration was low and within a range of 0.01 and 0.10 mg/l.

The influent cadmium concentration was increased to 6.60 mg/l, the effluent soluble cadmium concentration was slightly higher than for previous dosages and ranged between 0.11 and 0.16 mg/l, with an average of 0.13 mg/l. When the unit received cadmium at a dosage of 9.20 mg/l, the effluent soluble cadmium concentration rose and ranged between 0.13 and 0.51 mg/l with an average of 0.30 mg/l. In contrast to previous dosages, when the system was subjected to a cadmium dosage of 17.28 mg/l, the effluent soluble cadmium concentration fluctuated considerably and ranged between 0.25 and 1.17 mg/l (averaging 0.62 mg/l).

Figure 34 presents a rapid phase of cadmium uptake which is followed by a slower uptake at cadmium dosages of 4.14, 9.20, and 17.28 mg/l. At each dosage level the cadmium concentration in the sludge reached an equilibrium level at the end of the slower uptake phase. Two different rates of uptake (a rapid uptake followed by a slower uptake) have been reported by previous workers (20, 30, 40, 57). For influent cadmium concentrations of 4.14, 6.60, 9.20, and 17.28 mg/l, sludge cadmium concentrations reached 17.5, 20.0, 41, and 75 mg cadmium per gram dry weight of sludge, respectively.

Table XXI provides a summary of the operating characteristics (in terms of soluble cadmium) of the systems which operated at three different SRT's (3, 6, and 20 days) and various influent cadmium concentrations. Influent cadmium concentrations of 4.06, 6.02, 9.67, and 21.60 mg/l were removed up to 93.8, 96.3, 96.8, and 94.8 percent, respectively, by the 3 day SRT system. The results show that the 6 day SRT unit which received cadmium concentrations of 1.27, 4.27, and 6.36 mg/l produced cadmium removal efficiencies of 95.3, 94.4, and 92.1 percent, respectively. Cadmium removal efficiencies for the 20 day SRT unit were 98.3, 98.0,

TABLE XXI

CADMIUM REMOVAL EFFICIENCIES

		SRT = 3 days				SRT = 6 days			SRT = 12 days			
		Influent Cadmium (Cd) (mg/l)				Influent Cadmium (Cd) (mg/l)			Influent Cadmium (Cd) (mg/l)			
		4.06	6.02	9.67	21.60	1.27	4.27	6.36	4.14	6.60	9.20	17.28
Heavy Metal Removal	N	17	8	22	22	8	21	20	45	9	36	55
	Range	0.15-0.46	0.12-0.22	0.22-0.58	0.25-3.98	0.06-0.06	0.16-0.36	0.14-0.93	0.01-0.10	0.11-0.16	0.13-.51	0.25-1.17
Soluble Effluent (mg/l)	Mean	0.25	0.19	0.36	1.12	0.06	0.24	0.50	0.07	0.13	0.30	0.62
	S.D.	0.08	0.03	0.12	0.93	0.00	0.06	0.27	0.02	0.02	0.12	0.16
Removal Efficiency %		93.8	96.3	96.8	94.8	95.3	94.4	92.1	98.3	98.0	96.7	96.4

96.7, and 96.4 percent at influent cadmium concentrations of 4.14, 6.60, 9.20, and 17.28 mg/l, respectively. Effluent soluble cadmium concentrations were proportional to influent cadmium concentrations as dosages were increased from low (4.14 mg/l) to high (17.28 mg/l) concentrations. Compared to the 3 day and 6 day SRT systems, the 20 day SRT system produced an effluent with a lower cadmium concentration, which indicates higher removal efficiency.

Combined Metal Studies

Figures 35 and 36 show performance data for a 3 day SRT activated sludge system which was acclimated to lead. Seventeen days after the system was exposed to 16.03 mg/l lead, 1.02 mg/l zinc was added in addition to the lead. This is shown as day 42 on Figure 35. The zinc addition had no apparent impact upon effluent suspended solids or effluent soluble COD. The most notable effect of the zinc addition appeared to cause increased effluent soluble lead concentration (increasing from an average of 0.16 mg/l to an average of 0.31 mg/l). Effluent soluble zinc concentrations here were comparable to that observed at comparable zinc dosage during the single metal addition.

On day 56 of the study, 1.23 mg/l cadmium was added in addition to 16.03 mg/l lead and 1.02 mg/l zinc. Although no significant changes were observed for MLSS and effluent suspended solids concentrations, it was found that effluent soluble COD increased from 35 mg/l to 100 mg/l. Effluent soluble lead and zinc were not affected by 1.23 mg/l cadmium addition, and effluent soluble cadmium concentration was similar to that observed during the addition of cadmium alone at comparable cadmium dosages.

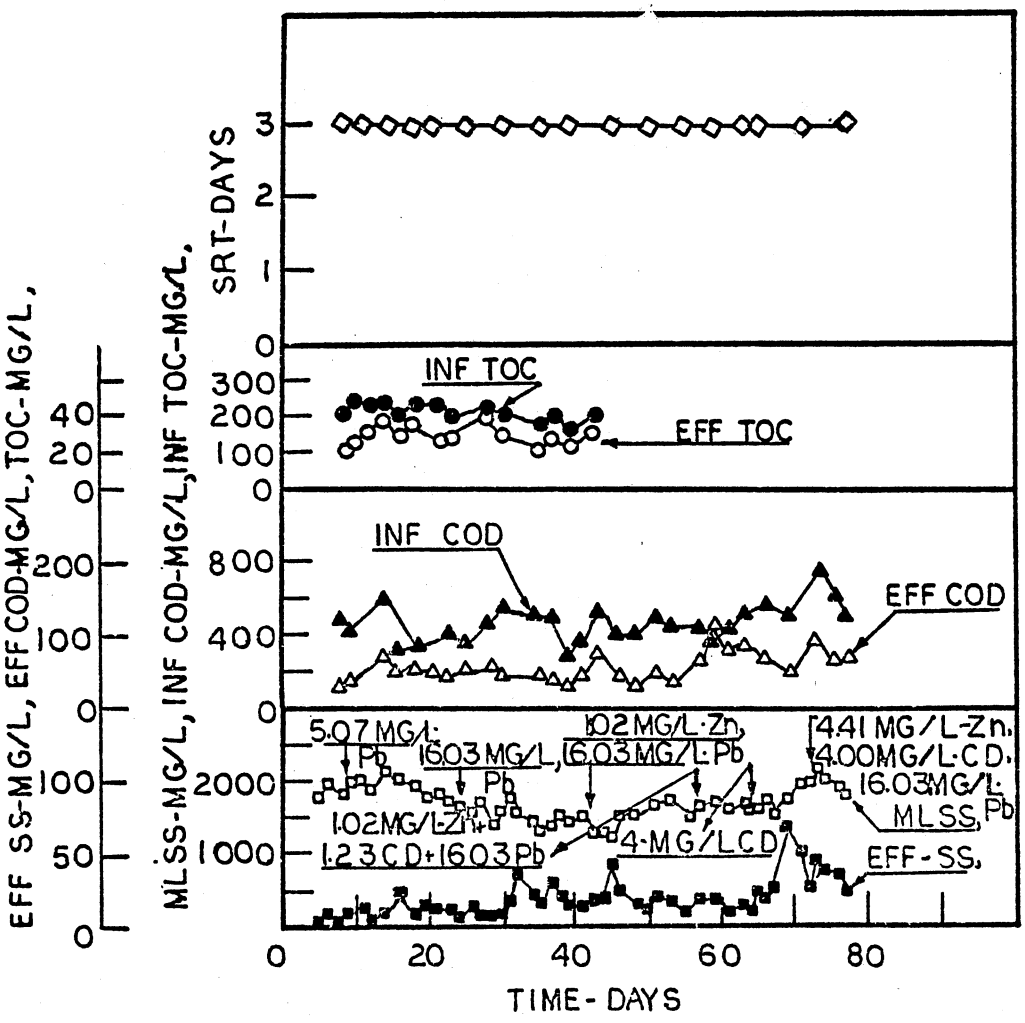

Figure 35. Performance Data for an Activated Sludge Reactor Maintaining at an SRT = 3 Days Receiving a Wastewater Composed of a Mixture of Metals

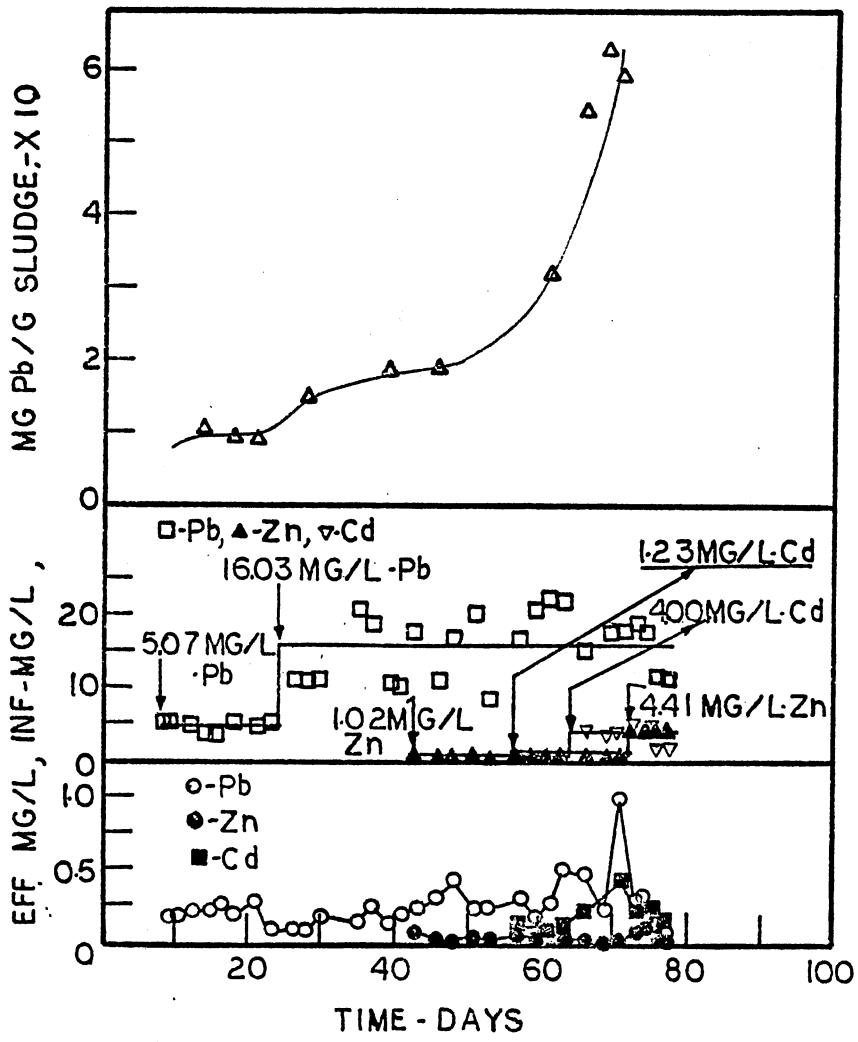

Figure 36. Influent, Effluent Soluble and Metal Uptake by the Activated Sludge Unit Operated at an SRT of 3 Days

On day 64 of the study, 4 mg/l cadmium was administered to 16.03 mg/l lead and 1.02 mg/l zinc. Due to the addition of 4 mg/l cadmium, the effluent suspended solids concentration increased. Effluent soluble zinc concentration was not affected by increasing cadmium concentration. However, effluent soluble lead concentration increased from an average of 0.31 to 1.00 mg/l, and effluent soluble cadmium concentrations increased from 0.15 to 0.45 mg/l.

On day 72 of the study, 4.41 mg/l zinc was added to the 16.03 mg/l lead and 4 mg/l cadmium. The addition of 4.41 mg/l zinc appeared to reduce the level of suspended solids concentration in the effluent. When zinc concentration was increased to 4.41 mg/l, the effluent soluble lead was reduced from 1.00 to 0.10 mg/l, and effluent soluble zinc concentrations were the same as the unit that received zinc individually.

The foaming problem that was observed when cadmium only was added at 3 day SRT did not appear when the system was acclimated to lead first.

During the entire study, the SRT was accurately maintained at 3 day. Figure 28 shows the 12 day SRT system which was acclimated to lead. On day 142 of the study, 10.56 mg/l zinc was added to the system already subjected to the 19.26 mg/l lead. Effluent soluble lead decreased from about 2.0 mg/l to 0.3 mg/l, and effluent zinc ranged between 0.27 and 0.47, which is approximately thirteen times higher than when zinc was added individually to the system which was acclimated to zinc only.

Metal Material Balances

Metals added to the activated sludge systems can be either adsorbed onto or into the sludge, or may pass through the system in the effluent. Materials balances were calculated for each of the activated

sludge system operated. Balances were made by calculating the mass of metal administered to the unit and also analyzing the mass of metal leaving the unit in both waste sludge and effluent. The period selected for conducting the mass balances followed the initial metal dosage increase during the time when system operation was stabilized. Mass balances were computed using the following equation:

Mass of metal inflow to the reactor = Mass of metal outflow from the system + Mass of metal accumulated into the sludge

$$M_I F = M_e F + M_s Xe F + M_s W_v + \frac{dM_s}{dt} XV$$

where

M_I = influent metal concentration, mass per volume

F = flow rate, volume per time

M_e = effluent metal concentration, mass per volume

M_s = sludge metal concentration, mass of metal per mass dry weight sludge

Xe = effluent suspended solids concentration, mass per volume

W_v = sludge wasted, mass per time

X = MLSS concentration, mass per volume

V = total reactor volume

$\frac{dM_s}{dt}$ = rate of metal uptake, mass per time

The results of the mass balances are presented in Table XXII.

TABLE XXII

METAL RECOVERY (percent)

Metal	SRT	Recovery (percent)
Lead	3	95.47
Lead	6	74.14
Lead	12	91.58
Zinc	3	91.58
Zinc	6	92.84
Zinc	6	72.62
Cadmium	3	94.50
Cadmium	6	99.79
Cadmium	12	91.16

Comparison of the Systems with the Same SRT (3 day) Receiving Different Initial and Rate of Increase in Cadmium Dosages

Figures 37 and 38 present performance data, influent, effluent, and sludge concentrations for a 3 day SRT unit which was subjected to influent cadmium concentrations of 1.27, 9.55, and 22.49 mg/l.

Figure 37 shows that the reactor was maintained at a constant SRT of 3 days. Comparison of the unit which was acclimated to low dosage (1.27 mg/l) cadmium and the unit that was acclimated to high concentration (Figure 13 - 4.06 mg/l), shows that effluent suspended solids concentrations of the unit that received 1.27 mg/l fluctuated less than the unit that was subjected to influent concentration of 4.06 mg/l.

A more drastic increase in the effluent soluble cadmium concentration

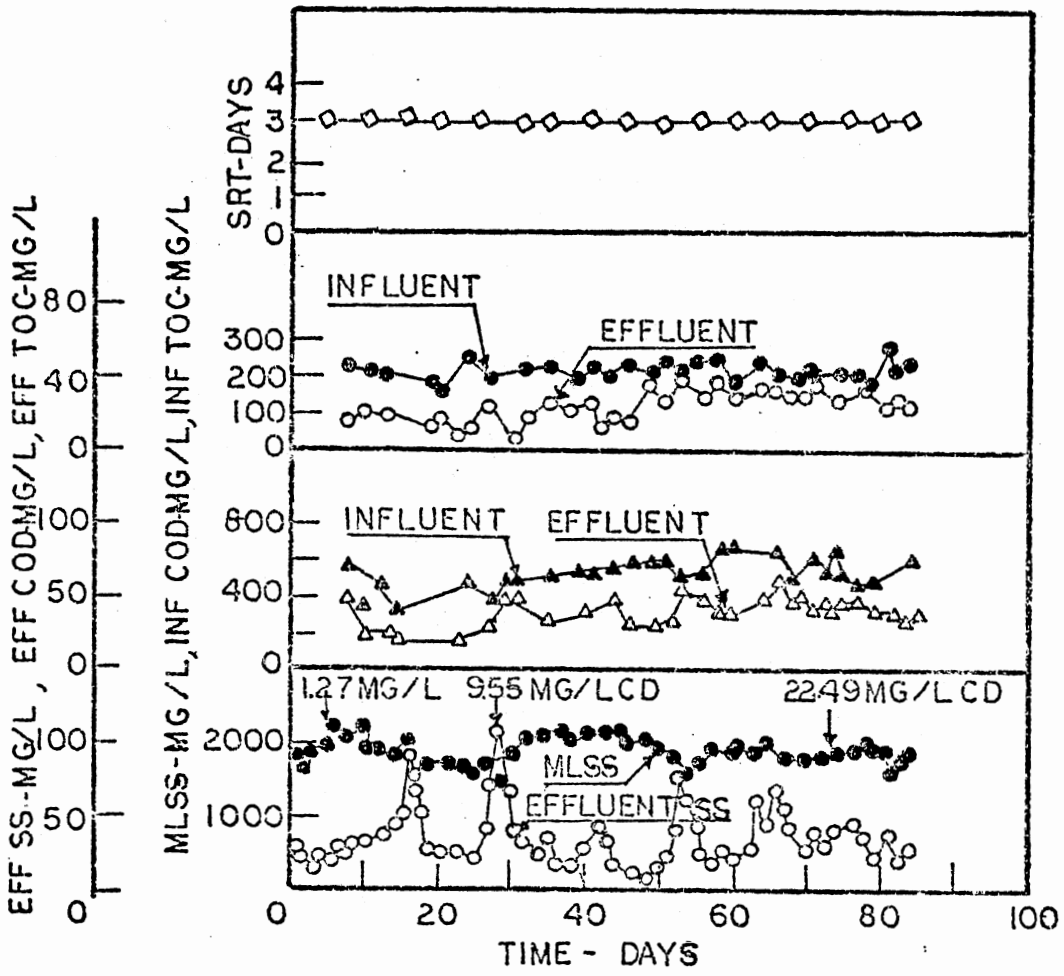

Figure 37. Performance Data for an Activated Sluge Reactor Maintaining at an SRT = 3 days Receiving a Wastewater Composed of Cadmium.

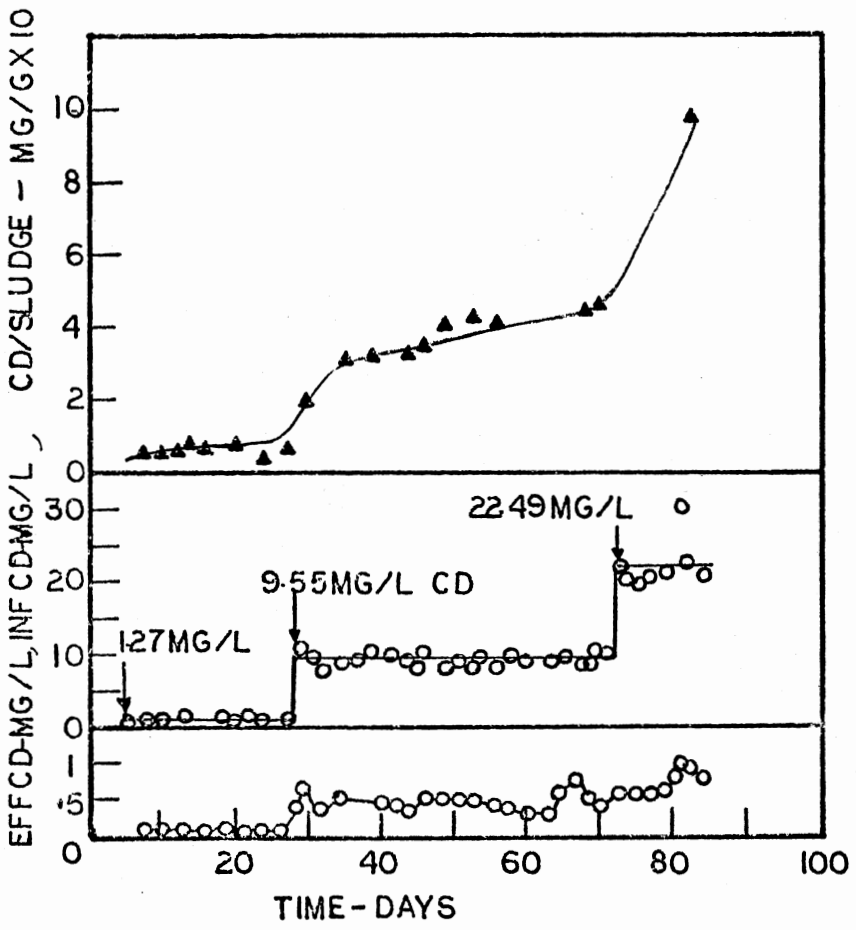

Figure 38. Influent Cadmium, Effluent Soluble Cadmium and Uptake by the Activated Sludge Unit Operated at an SRT of 3

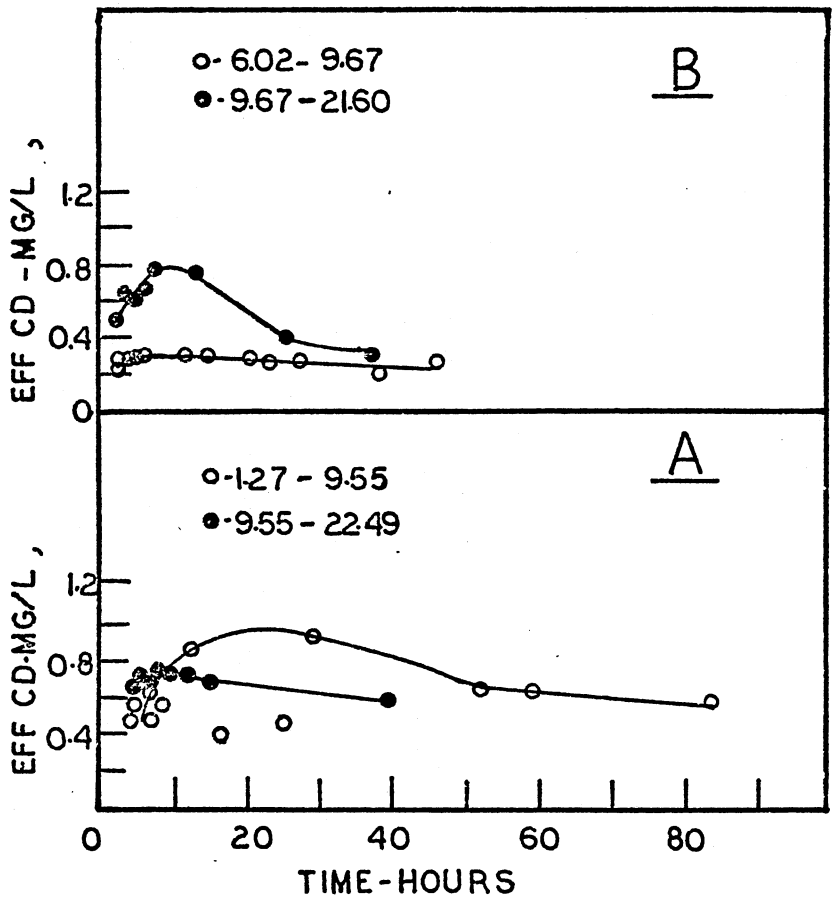

Figure 39. The Response of the Systems With the Same SRT (3 days) Receiving Different Initial and Rate of Increase in Cadmium Dosages

(0.12 to 0.80 mg/l) occurred when the influent cadmium concentration increased from 1.27 to 9.55 mg/l than when it increased from 6.02 mg/l to 9.67 mg/l, at which time effluent concentration increased from 0.22 to 0.60 mg/l.

The short term impact of cadmium shock loads is presented in Figure 39 (part A), which illustrates the response of the 3 day SRT unit to two cadmium shock loads (1.27 to 9.55 mg/l) and (9.55 to 22.49 mg/l). Figure 39 (part B) shows the response of the 3 day SRT unit which was subjected to step increases in cadmium concentration of 4.06 to 6.02 mg/l, and 6.02 to 9.67 mg/l, then from 9.67 to 21.60 mg/l. Comparison of Figure 39 (part A) and 39 (part B) shows that the most obvious observation made during the shock load study was soluble cadmium leakage into the effluent. No significant cadmium leakage was noted when influent cadmium concentrations increased from 6.02 to 9.67 mg/l (Figure 39 part B). Cadmium leakage observed for the 1.27 to 9.55 mg/l shock load (Figure 39 part A) were relatively high in magnitude (from 0.45 to 0.90 mg/l) and long duration (80 hours). An increase in influent cadmium dosage from 9.67 mg/l to 21.60 mg/l (Figure 39 part B) was relatively high in magnitude (from 0.50 to 0.80 mg/l) and short duration (35 hours) while increasing in influent cadmium concentrations from 9.55 to 22.49 mg/l (Figure 39 part A) was lower in magnitude (from 0.60 to 0.76 mg/l).

CHAPTER V

DISCUSSION

The purpose of the study was to observe and attempt to explain the fate of selected heavy metals (Pb, Zn, and CD) and their effect on the activated sludge systems.

Effect on the Effluent Quality With Respect to COD and TOC

Lead

Leakage of soluble substrate (in terms of COD and TOC) in the fluent was observed immediately following a step increase in influent lead concentrations at a SRT of 3 days. No detectible leakage was observed for the 12 day SRT unit following stepwise increases in invluent lead concentrations until 21 days after the addition of 19.26 mg/l lead to the system. This indicates that systems operated at higher SRT are more resistant to lead shock loads. It was found after the biomass became acclimated to lead, effluent soluble substrate concentrations were restored to previous levels except for the 6 day SRT unit (influent lead at 0.44 mg/l) and the 12 day SRT at high influent lead dosages (19.26 mg/l). The reason for the 12 day SRT system failure may be attributed to the fact that lead concentrations built up to toxic levels under the slower growth conditions. This claim is substantiated by the fact that a suppression (11.6% to 25.2%) in oxygen uptake rate was noted

for the 12 day SRT unit exposed to high influent lead concentrations while high influent lead concentrations had less impact upon oxygen uptake rate on the 3 day SRT unit.

Zinc

The results of this phase of the study indicated that neither effluent soluble TOC nor effluent soluble COD of the 3 day SRT unit were sensitive to step increases in the influent zinc concentration except at the dosage of 4.43 mg/l. This finding is further supported by the fact thata suppression (17.7%) in oxygen uptake rate was observed for the same unit at the dosage of 4.43 mg/l. No detectible leakage was observed for the 12 day SRT unit following stepwise increases in influent zinc concentrations up to 8.29 mg/l. This claim is verified by the fact that 22.1 percent reduction in the oxygen uptake rate was noted for the same system subjected to influent zinc concentrations of 8.29 mg/l, while high influent zinc concentrations(9.42 mg/l) was found to have a slight impact (4.4% reduction) upon the oxygen uptake rate for the 3 day SRT unit. The reason for this difference (more reduction in oxygen uptake rate at 4.43 mg/l zinc than 9.42 mg/l was observed) may be due to the predominance changes in the 3 day SRT unit. The 6 day SRT unit experienced a loss in solids after two weeks of operation at an influent zinc dosage of 1.83 mg/l. Since the unit was able to remove influent substrate efficiently (94% removal efficiency) and the oxygen uptake did not change, it would seem that the loss in solids was due to a change in bacterial predominance rather than a toxic effect.

Cadmium

Leakage of soluble substrate (in terms of COD and TOC) compared with the control system (48 mg/l of the COD and 20 mg/l of the TOC) was significant (71 mg/l of the COD and 29 mg/l of the TOC) throughout the 4.06 mg/l influent dosage for the SRT 3 day unit. Effluent soluble, in terms of COD, for the 3 day SRT was independent of the step increases in influent cadmium concentration (from 6.02 to 21.60 mg/l). No detectible leakage compared to the control system was observed for the 6 day SRT unit following stepwise increases in influent cadmium concentrations. However, there was remarkable leakage two weeks after increasing the dosage to 6.36 mg/l. No detectible leakage compared to the control system was seen for the 20 day SRT unit following stepwise increases in influent cadmium concentrations. For seven weeks of operation at an influent cadmium concentration of 17.28 mg/l, the system experienced no obvious leakage of substrate. After this initial acclimation period, the effluent substrate concentration, in terms of TOC, increased from 10 to 45 mg/l.

The reason for the 20 day SRT reactor failure may be attributed to the fact that cadmium dosages built up to toxic levels under slower growth conditions. This claim is substantiated by the fact that a suppression of 38.4 and 26.1 percent in the oxygen uptake rate in comparison with control values was noted for the 20 day SRT unit subjected to high influent cadmium dosage (9.20 and 17.28 mg/l), whereas the influence of influent cadmium concentrations of 9.67 and 21.60 mg/l on the oxygen uptake rate for the 3 day SRT system was less than the 20 day SRT unit (27.4% and 7.6% reduction in oxygen uptake rate for 9.67 and 21.50 mg/l, respectively).

Effect of Metal on Settleability and Dewaterability of the Activated Sludge System

Lead

Effluent suspended solids concentrations for the 3 day SRT unit were found to increase immediately following administrations of 5.46 and 18.08 mg/l dosages. Effluent suspended solids concentrations for the 12 day SRT unit were not impaired by increasing influent lead concentrations less than 19.26 mg/l. Based upon the comparison with control units, the settleability of the 3 day SRT system was adversely affected by influent lead addition, whereas the settleability of the 12 day SRT system remained good at influent lead concentrations greater than 0.57 mg/l.

Zinc

Effluent suspended solids concentrations for the 3 day SRT unit were found to increase immediately following the addition of 4.43 mg/l zinc, and gradually increased at an influent zinc concentration of 9.42 mg/l. At the dosage of 9.42 mg/l, there might have been a change in predominance resulting in a dispersed type of biomass resulting in an increase in effluent solids concentrations. Effluent suspended solids concentrations for the 12 day SRT unit decreased after increasing the zinc concentration greater than 1.03 mg/l.

Based upon a comparison with the control units, the settleability of the 3 day SRT and 6 day SRT systems were reduced by increasing zinc concentrations while the settleability of the 12 day SRT unit was enhanced as influent zinc dosages increased. On the basis of CST tests

the sludge dewaterability was reduced about 11 to 39 percent, increasing influent zinc concentrations for 3, 6, and 12 day SRT systems.

Cadmium

Effluent suspended solids concentrations for the 3 day SRT unit were found to increase several days after the addition of influent cadmium dosages of 4.06, 9.67, and 21.60 mg/l. Effluent suspended solids concentrations for the 6 day SRT unit were observed to increase several days after the addition of influent cadmium concentrations of 4.27 and 6.36 mg/l. Effluent suspended solids concentrations for the 20 day SRT system were not affected by increasing influent cadmium concentrations of 4.14, 6.60, and 9.20 mg/l.

Based upon the comparison with the control systems generally, the settleability of the 3 day, 6 day, and 20 day SRT units was diminished as influent cadmium concentrations increased.. Increasing influent cadmium concentrations reduced (19 to 68 percent compared with control values) the dewaterability of sludge for the 3, 6, and 20 day SRT units. This indicates that changes in characteristics of the biomass did occur.

Fate of Metals

Lead

Effluent soluble lead concentrations for the 3 day SRT unit were found to increase dramatically immediately following step increases in influent lead concentrations. After several days, effluent soluble lead concentrations generally returned to the previous level. The 12 day SRT unit effluent soluble lead concentrations were not noticeably impaired by increasing influent dosages until the 19.26 mg/l lead dosage was

applied. At this time, effluent soluble lead concentrations increased and remained at elevated levels. With the exception of influent lead concentration of 19.26 mg/l, effluent soluble lead concentrations for the 12 day SRT unit were lower than that observed for the 3 day SRT unit at corresponding influent lead dosages. Based upon influent, effluent and sluge analyses, mass balances indicated that most of the influent lead (greater than 92%) was found in the sludge.

The accumulation of the lead in the sludge could create potential problems for the ultimate disposal. Lead is listed as one of the criteria for the EPA toxicity test. Leaching of lead from the landfield sludge could possibly be a problem.

Zinc

The 3 day SRT unit effluent soluble zinc concentration was increased as zinc concentrations increased from 1.14 to 9.42 mg/l. Sudden increase in the effluent soluble zinc was observed after addition of influent zinc concentrations of 9.42 mg/l for the 3 day SRT unit. At this time, effluent soluble zinc dosages remained at elevated levels. Effluent soluble zinc concentrations for the 6 day SRT system were found to remain at the same levels during the entire addition of influent zinc dosage of 1.83 mg/l. Effluent soluble zinc concentrations for the 12 day SRT unit were found to increase dramatically immediatly following addition of influent zinc at dosages of 1.03 and 37.63 mg/l. No significant leakage of the effluent soluble zince was observed upon step increase in influent zinc concentrations from 3.96 to 20.17 mg/l at SRT of 12 days. Effluent soluble zinc concentrations for the 12 day SRT unit were lower than for the 3 day SRT unit at corresponding

influent zinc concentrations. The results indicate that zinc can be removed more efficiently by higher SRT units. Based upon influent, effluent and sludge zinc analyses mass balances indicated that most of the influent zinc (greater than 72.62%) was found in the sludge. Since zinc is not listed as a hazardous pollutant, accumulation of the zinc in waste sludge should not be a major concern.

Cadmium

Effluent soluble cadmium concentrations for the 3 day SRT unit were affected by increasing influent cadmium concentrations. The 6 day SRT system effluent soluble cadmium concentration was markedly affected by increasing influent cadmium dosages. The 20 day SRT reactor effluent soluble cadmium concentration was noticeably affected as influent cadmium concentrations increased. The increase in effluent soluble cadmium for the 6 and 20 day SRT units was found to be directly proportional to increase in the influent concentration. Effluent soluble cadmium concentrations for the 20 day SRT unit were lower than dosages seen for the 3 day and 6 day SRT reactors at corresponding influent cadmium concentrations. On the basis of influent, effluent and sludge cadmium analyses, mass balances indicated that most of the influent cadmium (greater than 74.14 percent) was obtained in the sludge. Like lead, cadmium is one of the criteria for EPA toxicity tests. Potential problems in disposal could result with this metal.

Effect of Metal on Biokinetic Constants

Examples of the plots used to determine the biokinetic constants are shown in Figures 16 through 25. The plots based on the Lawrence

and McCarty (Figures 20 and 21), and Eckenfelder (Figures 22 and 23) models were found to be subjected to much data scatter. Because of this, many lines with different slopes and intercepts may be drawn through these data with each line being used to describe the data. This same kind of scatter was also seen on other plots which were employed to determine biokinetic constants for the synthetic wastewater containing heavy metal. The Kincannon and Stover design model (Figures 16 and 17) eliminate scatter, gives greater engineering confidence, and generally provides a more conservative design (68).

U_{max} and k_B in terms of COD and TOC were affected upon addition of lead to the synthetic wastewater. The most significant change in true cell yield (Y_t) based on COD occurred when the system received a dosage of 3.32 mg/l lead. Decay coefficient (k_d) values, in terms of COD and TOC, were affected by addition of lead. The values of ké were not affected significantly by the addition of lead to the systems. Significant effects were observed on k and k_s (in terms of COD and TOC) while lead was administered to the synthetic wastewater when compared with control values.

It was found that addition of zinc to the system had noticeable effects on k_B and U_{max}, in terms of COD and TOC. A significant increase in k_d, in terms of COD and TOC, occurred at a zinc dosage of 1.14 mg/l and at 4.43 mg/l in terms of TOC. True cell yield (Y_t) values were not affected by addition of 1.14 and 4.43 mg/l of zinc. k and k_s values, in terms of COD, increased as zinc was added at a dosage of 4.43 mg/l compared with control values. The addition of zinc at a dosage of 1.14 mg/l did not have a significant effect on ké in terms of COD when compared with control values. Further increase in zinc concentrations did

not have an obvious effect on k_e', in terms of COD and TOC, when compared with the control system.

Addition of cadmium caused k_B and U_{max} values (in terms of COD) to become lower than control values. The lowest values of k_d were found at influent concentrations of 9.67 in terms of COD and 1.27 mg/l in terms of TOC. The influent cadmium concentration of 9.67 mg/l caused no effect on Y_t values (in terms of COD and TOC). However, the most obvious effect of cadmium on Y_t, in terms of COD and TOC, occurred at a loading of 6.02 mg/l. The lowest values of k and k_s, in terms of COD and TOC, were found to be at the influent concentration of 4.06 mg/l, and the highest values of k_s, in terms of COD and TOC, were found at 9.67 mg/l cadmium. The most significant effect of cadmium on k_e' in terms of TOC occurred at a dosage of 4.06 mg/l.

As previously mentioned, it would be difficult to reach a conclusion that variations in k_e', k, and k_s as calculated by the methods of Eckenfelder, and Lawrence and McCarty were due to the type of metal, dosages of metal, or a shift in microbial species. However, by using the Kincannon and Stover design model to calculate the biokinetic constants, U_{max} and k_B, scatter in the data is eliminated and changes in the performance of the activated sludge system are, therefore, more positively identified.

General Discussion

The results of this work indicated that a very high metal removal efficiency (greater than 84%) was achieved when the systems received the heavy metals (Cd, Pb and Zn). However, this rate of efficiency may not be obtained for those metals which were not examined during this

study. For example, studies conducted at the Oklahoma State University Bioenvironmental Engineering Laboratories on nickel-containing industrial wastewaters showed that 40 to 50 percent of the influent nickel could be removed by the activated sluge system.

The 6 day SRT unit was not operated successfully compared with lower (3 day SRT) and higher SRT (12 and 20 days) systems when heavy metals (Pb, Zn and Cd) were added. During the past two years of biokinetic research at the OSU Laboratories, similar failures have been experienced by the author with other 6 day units fed industrial wastewaters (69). This work suggests to design engineers that it would be on the safer side if they do not design or operate a wastewater treatment plant at a 6 day SRT. As mentioned previously, the loss in solids for a 6 day unit which was exposed to Cd, Zn or Pb may not be due to the toxicity effect of heavy metal on the biomass. This statement was confirmed by microscopic examination and oxygen uptake rate. Microscopic examinations indicated that the protozoa disappeared several days after addition of heavy metal. There was no significant change in oxygen uptake rate.

It can also be noted that MLSS concentrations in the 3 day SRT reactor were reduced when the unit was subjected to heavy metal, and it occurred every time the heavy metal was increased. This could be due to change in the cell yield of the biomass. This phenomenon was observed at the OSU Bioenvironmental Engineering Laboratories when the 3 day SRT unit was exposed to nickel. However, the reduction of MLSS concentration was not noted for 10, 12, and 20 day SRT systems.

Aerobic or anaerobic digestion of sludge could potentially release the metal that was adsorbed onto or into the sludge back into solution.

Return of these metals into the solution could conceivably impact the digestion process adversely. However, this aspect was beyond the scope of this study.

CHAPTER VI

CONCLUSIONS

The following conclusions were drawn from this work:

1. Addition of lead in the form of lead acetate at 3 and 6 days SRT did not affect COD removal efficiency. However, it caused a two percent reduction in COD removal efficiency at 12 day SRT.

2. The activated sludge systems receiving wastewater containing lead as lead acetate at concentrations ranging between 0.56 to 19.26 mg;l removed 84.1 to 99.4 percent of the metal.

3. The activated sludge systems receiving wastewater containing zinc as zinc acetate were found to experience no effect in removal efficiencies in terms of COD and TOC.

4. The results of the study showed that the activated sludge process could remove more than 96.5 percent of the zinc at 3, 6, and 12 day SRT.

5. Addition of cadmium as cadmium acetate at 6 day SRT did not have any impact on the COD removal efficiency. However, addition of cadmium at 3 day SRT had a slight influence on COD removal. No effect was observed upon addition of 4.14, 6.60 and 9.20 mg/l cadmium at 20 day SRT except at 17.28 mg/l.

6. The results of the study indicated that cadmium was removed up to 98.3 percent by the activated sludge system.

7. The 3 and 12 day SRT units could tolerate higher concentrations

than those at 6 day SRT for all three metals (Zn, Pb, and Cd).

8. Increasing the influent lead dosages has more effect on sludge settleability than increasing influent cadmium and zinc dosages. However, an improvement in sludge settleability was observed at 12 day SRT, while zinc was added to the system.

9. The results indicated that the major removal mechanism of heavy metals in the activated sludge system is due to the accumulation of heavy metals in the sludge.

CHAPTER VII

SUGGESTIONS FOR FUTURE WORK

As a result of observations during the experimental work, the following suggestions are made for further study:

1. Leaching of heavy metals from the activated sludge should be studied in more detail. For those metals listed as hazardous materials, the leaching of those metals from waste sludge in sufficient concentrations could make it difficult to dispose of the waste sludges in a land field.

2. More study regarding the effect of sludge metal concentrations on aerobic or anaerobic digestion should be made.

3. Since temperature and pH may have an effect on metal toxicity, the unit can be operated at different degrees of temperature and pH.

4. Different organic loadings should be applied to determine whether or not they have an effect on metal removal.

5. Further studies need to be conducted to determine the causes of instability of 6 day SRT reactor.

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